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ON OSMYL-DITETRAMIN.

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My researches on the metals of the platinum group were interrupted many years since by the want of a laboratory in which the separation and collection of osmic hyperoxide, OsO_4, could be effected without serious danger to the air-passages and to the eyes. As I may not be able to take up the subject again, I will here give the results of my study of a peculiar compound of osmium, oxygen, and the elements of ammonia, of much interest from a theoretical point of view.

In 1844[1] Frémy described a yellow crystalline substance which he obtained by adding ammonic chloride to a solution of potassic osmate, and to which he gave the formula,

$$2NH_4Cl.OsO_3.(NH_3)_2,$$

representing its formation by the equation,

$$OsO_4K_2+4NH_4Cl=2NH_4Cl.OsO_3.(NH_3)_2+2KCl+2H_2O.$$

In examining this salt I found that it gave a crystalline compound with platinic chloride, and a further study showed that it yielded

[1] Annales de Chimie et de Physique, 3d Series, 12, 522.

by double decomposition with salts of silver a well-defined crystalline sulphate, nitrate and oxalate. I therefore[1] proposed for it the formula,

$$4NH_3.OsO_3.Cl_2.$$

According to this view the formation of the salt may be represented by the equation,

$$4NH_4Cl+OsO_4K_2=4NH_3.OsO_3.Cl_2+2KCl+2H_2O.$$

The subject was taken up some time after by Claus,[2] who ascribed to the chloride the formula,

$$4NH_3.OsCl_2+2H_2O,$$

so that it would be the osmium analogue of well-known compounds of palladium, platinum, iridium and ruthenium. If this view be correct, the formation of the salt would be represented by the equation,

$$4NH_4Cl+OsO_4K_2=4NH_3.OsCl_2+2KCl+2O+2H_2O.$$

It will be seen that Claus's formula requires that free oxygen should be given off in the formation of the chloride. In repeated preparations I have never found this to be the case. On Claus's view the chloride contains two molecules of water of crystallization. According to all analogy this water should be given off at a temperature below that at which decomposition of the salt itself takes place. To determine this point I heated a portion for an hour to successive temperatures of 100°, 115°, 130°, 140° and 154° C. The total loss after the five hours was 0.59 per cent., the salt being in appearance slightly decomposed. A loss of one molecule of water only would correspond to 4.84 per cent. These facts appear to me to show that the formula which I proposed is correct. Frémy's view would scarcely be defended by any chemist at the present time.

I propose to call the complex $OsO_3.4NH_3$, which we may for the sake of convenience consider as an integral part of each salt in the series, osmyl-ditetramin, to distinguish it from osmio-ditetramin, $Os.4NH_3$, which remains to be discovered, and which would correspond to the palladium, platinum, ruthenium and iridium salts above referred to.

[1] American Journal of Science, 2d Series, **25**, 248. [2] N. Petersb. acad. Bull. **1**, 121 and **6**, 179.

Chloride of Osmyl-ditetramin. When concentrated solutions of sal-ammoniac and potassic osmate are mixed, an orange-yellow crystalline precipitate of the chloride of osmyl-ditetramin usually separates at once. The potassic osmate should be added in small excess, and the salt after precipitation washed with cold water and dried *in pleno* over sulphuric acid. It is slightly soluble in cold water; hot water readily dissolves but soon decomposes it, with evolution of free osmic hyperoxide, OsO_4, and precipitation of a black powder. Strong chlorhydric acid precipitates the chloride from its solutions as a crystalline yellow or orange-yellow powder. The salt may be dissolved in hot water containing a little chlorhydric acid, and gives a deep orange-yellow solution, from which it separates, on cooling, in small deep brown-yellow crystals. The chloride is completely decomposed by ignition, leaving pure metallic osmium as a grey porous mass. It is necessary, however, as Frémy has stated, to ignite in a current of hydrogen to avoid loss by the formation of osmic hyperoxide. The decomposition by heat is expressed by the equation,

$$OsO_2.4NH_3.Cl_2 = Os + 2NH_4Cl + 2H_2O + 2N,$$

and furnishes perhaps the most simple and convenient method of obtaining pure metallic osmium. To prevent oxidation completely the osmium should be heated to a high temperature, and allowed to become cold in a current of hydrogen, which must afterward be displaced by carbonic dioxide and finally by air. Finely divided osmium oxidizes easily in the air, giving off vapors of osmic hyperoxide. It also exhibits in a remarkable degree the property possessed by spongy platinum, of causing the combination of oxygen and hydrogen, but the osmium is oxidized at the same time. This fact lends some support to the chemical theory of the action of platinum under the same circumstances.

Of the chloride:

0.7850 gram gave 0.4158 gram osmium = 52.96 per cent.

0.9520 gram gave 0.5065 gram osmium = 53.20 per cent.

0.6102 gram gave 80 cc. of nitrogen (moist) at 5° C. and 754.37 mm. = 15.87 per cent.

0.8667 gram gave 0.6813 gram AgCl = 19.45 per cent. chlorine.

1.1565 gram gave 0.3546 gram water = 3.46 per cent. hydrogen.

These analyses agree fairly well with the formula,

$$OsO_2.4NH_3.Cl_2,$$

which requires:

		Calc'd.	Found.		Calc'd.	
Osmium	199	53.78	53.20	52.96	53.15	194
2 Chlorine	71	19.19	19.45		19.45	71
12 Hydrogen	12	3.24	3.46		3.29	12
4 Nitrogen	56	15.14	15.89		15.34	56
2 Oxygen	32	8.65	...		8.77	32
	370	100.00			100 00	365

The osmium was determined by careful ignition in a current of hydrogen and afterward of carbonic dioxide. To estimate the chlorine, the salt was ignited with sodic carbonate and the reduced osmium separated by filtration.

Nitrogen was determined by Simpson's method, and hydrogen by combustion with oxide of copper. In judging analyses of this and similar compounds, it must be borne in mind that the salt is difficult to purify by repeated crystallization, on account of the facility with which it is decomposed, and also that the atomic weight of osmium is very uncertain. As will be seen, the analyses agree much better with the formula if we adopt for osmium the atomic weight proposed by Mallet,[1] 194, but I have not considered myself justified in changing the value generally received. Seubert[2] has recently shown that the atomic weights of platinum and iridium are lower than was supposed, and has suggested that the same is true in the case of osmium.

A solution of the chloride of osmyl-ditetramin gives with one of potassic ferro-cyanide a fine violet color. The reaction is very delicate, and affords the best method yet discovered for the detection of minute quantities of osmic hyperoxide in the wet way. In applying this test, the metal must first be oxidized. This may be easily effected by heating the alloy or compound of whatsoever kind in a silver crucible with caustic potash and potassic nitrate and then distilling the fused mass with nitric acid. The distillate is to be rendered alkaline by a small quantity of caustic potash, and then reduced to potassic osmate, OsO_4K_2, by a drop or two of alcohol or of a solution of potassic nitrite. A solution of ammonic chloride, sulphate or nitrate, is then to be added, after which potassic ferro-cyanide gives a more or less well-defined violet color. In this manner it is possible to recognize quantities of osmium too

[1] American Journal of Science, 2d Series, **29**, 55, 56.
[2] Wiedemann's Annalen, B. **207**, 1–50.

small to be detected by the characteristic odor of the hyperoxide.

Chlorplatinate. This salt is best prepared by boiling the finely pulverized chloride with a solution of platinic chloride. It forms beautiful orange-yellow crystals, slightly soluble in cold water.

Of this salt:

0.4800 gram gave 0.2608 gram osmium and platinum = 54.33 per cent., and 0.1308 gram platinum = 27.25 per cent., giving 0.1300 gram osmium by difference = 27.08 per cent.

The formula $OsO_2.4NH_3.Cl_2+PtCl_4$ requires 27.38 per cent. platinum and 26.82 per cent. osmium. In the analysis of this compound, the weight of the two metals was first obtained by reduction with hydrogen. The osmium was then volatilized by roasting the mixture in a current of oxygen at a red heat.

Sulphate. The sulphate, like the other salts of the series, is best prepared by pouring a solution of potassic osmate, OsO_4K_2, into a concentrated cold solution of ammonic sulphate. Its formation may be represented by the equation,

$$2SO_4(NH_4)_2+OsO_4K_2=OsO_2.4NH_3.SO_4+SO_4K_2+2H_2O.$$

The sulphate forms beautiful small crystals which have a fine orange-yellow color. It dissolves rather freely in hot, but slightly in cold water.

Of this salt:

0.7580 gram gave 0.3597 gram osmium = 47.45 per cent.

1.7484 gram gave 0.9933 gram SO_4Ba = 23.40 per cent. SO_4.

1.2396 gram gave 0.3972 gram water = 3.56 per cent. hydrogen.

0.6490 gram gave 0.2055 gram water = 3.51 per cent.

1.2067 gram gave 138 cc. nitrogen (moist) at 6.5 and 765.80 mm. = 13.99 per cent.

The analyses lead to the formula,

$$OsO_2.4NH_3.SO_4+H_2O.$$

		Calc'd.	Found.		Calc'd.	
1 Osmium	199	47.93	47.45		47.55	194
4 SO_4	96	23.36	23.40		23.53	96
14 Hydrogen	14	3.41	3.51	3.56	3.43	14
4 Nitrogen	56	13.62	13.99		13.72	56
3 Oxygen	48	11.68			11.77	48
	413	100.00			100.00	408

Nitrate. The nitrate is most easily prepared by pouring a solution of potassic osmate into a cold saturated solution of ammonic nitrate. The salt separates after a time in granular orange-yellow crystals which are paler in color than those of the sulphate. It is the least stable of the salts which I have examined, the cold solution being soon decomposed with evolution of free osmic hyperoxide.

Oxalate. The oxalate is the most stable salt which I have obtained. It is readily prepared by the process given for the other salts, employing of course ammonic oxalate. The salt separates in beautiful yellow or orange-yellow crystals, which are but slightly soluble in cold water. In this salt:

1.0345 gram gave 0.5133 gram osmium = 49.62 per cent.

1.1553 gram burnt with CuO gave 0.3441 gram water = 3.30 per cent. hydrogen and 0.2713 gram CO_2 = 6.40 per cent. carbon.

1.2817 gram gave 0.3834 gram water = 3.32 per cent. hydrogen.

1.8541 gram gave 234 cc. of nitrogen (moist) at 12.5° C. and 761.74 mm. = 14.94 per cent.

These analyses correspond tolerably well with the formula,

$$OsO_2.4NH_3.C_2O_4.$$

		Calc'd.	Found.		Calc'd.	
Osmium	199	51.19	49.62		50.78	194
C_2O_4	88	22.86	23.47		23.04	88
Hydrogen	12	3.11	3.30	3.32	3.14	12
Nitrogen	56	14.54	14.94		14.67	56
Oxygen	32	8.30			8.37	32
	387	100.00			100.00	382

As in the cases of the chloride and sulphate, the analyses correspond better with the assumption that the atomic weight of osmium is 194.

Claus obtained a solution of the oxide or hydroxide of osmyldiammin by digesting a solution of the chloride with argentic oxide. Jacoby first converted the chloride into sulphate by digestion with argentic sulphate, and then decomposed the sulphate with baryta water. The solutions thus obtained are yellow, alkaline, and very easily decomposed.

When a solution of potassic osmate is poured into a cold strong solution of hydrochloride of narcotin, cinchonin or strychnine, a

white precipitate is formed in either case which dissolves readily in dilute chlorhydric acid. The solutions give precipitates with platinic and auric chlorides. It seems at least possible that new bases are formed in which the higher alkaloids replace the ammonia of osmyl-ditetramin.

When a solution of potassic osmate is mixed with one of chloride of luteocobalt, $Co_2(NH_3)_{12}Cl_6$, a buff-colored precipitate is formed, which on addition of dilute chlorhydric acid becomes orange-yellow and beautifully crystalline. The salt dissolves in cold water without decomposition, but the solution is decomposed on gentle heating. It gives beautiful crystalline salts with auric and platinic chlorides. In the orange-yellow salt:

0.5647 gram gave 0.2642 gram cobalt and osmium = 46.70 per cent.

0.2642 gram of the mixed metals lost 0.2085 gram osmium as OsO_4 = 36.92 per cent., and gave by difference 0.0557 gram cobalt = 9.78 per cent.

0.4529 gram gave 52.5 cc. nitrogen (moist) at 17° C. and 765.9 = 13.51 per cent.

The ratios are here $OsCo_2N_{12}$, but further analyses are necessary to determine the constitution of the salt. The chlorides of the other cobaltamines also react with potassic osmate. My experiments in this direction were suggested by the reflection that the salts of the cobaltamines in certain points closely resemble the salts of ammonium.

When potassic osmate is mixed with a solution of the chloride of palladio-ditetramin, $Pd(4NH_3)Cl_2$, an orange-yellow or sherry wine colored solution is formed. The addition of chlorhydric acid throws down a fine orange-yellow crystalline precipitate. A solution of this salt gives an orange-yellow precipitate with platinic chloride.

The experiments detailed appear to show that interesting results will be obtained by pursuing the subject in the direction which I have pointed out. The very numerous class of metal amines offers a wide field for study.

I have also made some observations on other osmium bases which may be mentioned in this connection.

When ammonia is added to a solution of potassic osmate, the liquid immediately takes a sherry-wine color. After addition of an excess of chlorhydric acid and subsequent neutralization with

ammonia, the solution gives crystalline precipitates with ammonic oxalate, auric and mercuric chlorides, etc., and therefore contains a metalamine of some kind. As the osmiamines corresponding to platin-diamin, $Pt(NH_3)_2$, and platin-ditetramin, $Pt(NH_3)_4$, have not yet been obtained, it is possible that the base obtained by the action of ammonia upon potassic osmate may represent the osmium analogue of one of these.

The views of Blomstrand as to the constitution of the metalamines have found much favor with chemists, and appear to involve less that is purely hypothetical than any others which have been proposed. Applying this theory to the present case, it will be seen that osmyl-ditetramin chloride may be written either as

$$O_2{=}Os.4NH_3.Cl_2 \qquad O_2{=}Os\begin{cases} NH_3.NH_3{-}Cl \\ NH_3.NH_3{-}Cl \end{cases}$$

or as

$$Os{=}Os.4NH_3.Cl_2 \qquad Os\begin{matrix} O-NH_3-NH_3-Cl \\ O-NH_3-NH_3-Cl \end{matrix}$$

The first view requires us to consider the osmium as tetratomic, while according to the second formula it would be diatomic. If we consider the osmium as diatomic, the chloride ought to form addition products with iodine and bromine, as for instance,

$$Os\begin{matrix} I \\ O-NH_3-NH_3-Cl \\ O-NH_3-NH_3-Cl \\ I \end{matrix}$$

I have sought in vain to form such compounds, and therefore consider the first view as the more probable of the two.

Devillé and Debray[1] have shown that ruthenium forms a hyperoxide the formula of which is RuO_4, and which is therefore the analogue of the osmium compound. The close resemblance between the two metals suggests the possibility of forming a ruthenium series similar to that of osmium which I have described, but I have made no experiments to test this suggestion, which I throw out for what it may prove to be worth.

With respect to the nomenclature employed, I may here remark that upon Blomstrand's theory of the constitution of the metal amines, it is possible to distinguish different modes of combination of ammonia by names which are not too cumbrous for ordinary

[1] Comptes Rendus, **83**, 926.

use. Thus we have two series of platinamines which we may write respectively,

$$Pt\begin{matrix}\diagup NH_3—NH_3— \\ \diagdown NH_3—NH_3—\end{matrix} \quad \text{and} \quad Pt\begin{matrix}\diagup NH_3— \\ \diagup NH_3— \\ \diagdown NH_3— \\ \diagdown NH_3—\end{matrix}$$

In the first platinum is diatomic; in the second tetratomic. If we call the second "platino-tetramin," the first might be termed "platino-ditetramin," and in this manner the difference of atomicity, the number of atoms and the modes of combination of the ammonia are clearly expressed.

The experimental part of the work here published was finished long since. I[1] have delayed its publication in the hope of rendering it more complete, and especially of generalizing the results in various ways, some of which I have indicated above. The work is now given to the public, not as being complete or exhaustive, but simply in the hope that it will be found to contain suggestions which may be of use to other chemists working in the same direction.

CAMBRIDGE, *April 15th*, 1881.

NOTE ON THE COMPOSITION OF THE CARBONACEOUS RESIDUE FROM THE SOLUTION OF STEEL IN THE DOUBLE CHLORIDE OF COPPER AND AMMONIUM.

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While in charge of the laboratory of the U. S. Iron and Steel Commission at Watertown Arsenal, Massachusetts, in 1877, I was led to investigate the composition of the carbonaceous matter liberated from steel by the action of the double chloride of copper and ammonium; and as the results I obtained were at variance with those previously reported by others, I propose to give a short

[1] The first notice of the true character of Frémy's osmium salt was published jointly by Dr. F. A. Genth and myself (Am. Jour. Sci. *loc. cit.*). Circumstances prevented Dr. Genth from taking any part in the investigation, and I must therefore be held exclusively responsible for all that I have published upon the subject.—W. G.

account of them. I had hoped to follow up the work and present it in a more complete form; but as there seems to be no immediate prospect of my being able to do so, and as the work has remained untouched for four years, I venture to present these results, in the hope that they may be of assistance to some one following the same line of research.

Schützenberger and Bourgeois[1] treated white iron with copper sulphate, dissolved the precipitated copper in ferric chloride, filtered, washed, dried at 100°, and analyzed the carbonaceous matter with the following results:

Carbon	64.00
Water	26.10
Silicious Ash	8.10
Undetermined matter	1.80
	100.00

corresponding nearly to the formula $C_{22}.3H_2O$.

I used a steel of the following composition:

Sulphur	0.002	per cent.
Phosphorus	0.005	"
Silicon	0.095	"
Manganese	0.122	"
Cobalt	0.000	"
Nickel	0.000	"
Copper	0.010	"
Carbon	1.455	"

Drillings of this steel were treated with a large excess of the double chloride of copper and ammonium, and when all the copper first precipitated was redissolved, the carbonaceous matter was filtered off, washed with the double chloride acidulated with hydrochloric acid and finally with water, until the filtrate gave no precipitate with a crystal of silver nitrate.

It was then dried at a low temperature, thoroughly mixed in a platinum crucible, and kept for use in a desiccator. For the determination of carbon and hydrogen I used a glass tube 15 inches long and ½ in. in diameter. In the forward part about ½ in. from the cork of the calcium chloride tube was a piece of silver foil about

[1] Comptes Rend. 1875.

2 inches long, rolled tightly and completely filling the diameter of the tube; next to this 4 inches of coarse oxide of copper with an asbestos plug at either end.

A roll of copper wire thoroughly oxidized, 3½ in. long and of about the same diameter as the inside of the tube, came to within an inch of the back end of the tube, leaving a 3 in. space in the centre. The back end of the tube was connected by a perforated cork and glass tube with an oxygen holder and an air holder, so that dry pure oxygen or air could be passed through the apparatus at pleasure. The tube was placed in a gas combustion furnace 13 inches long, one inch of the tube projecting at each end.

About 0.2 gram of carbonaceous matter was put into a small platinum boat, and the boat into a glass test tube, the open end of which was provided with a cork covered with tin foil, to prevent access of air. This tube was then placed in an air bath heated to about 100° C. and the carbonaceous matter thoroughly dried. It was then taken from the bath, cooled in a desiccator and weighed. The tube, cork and empty boat having been previously weighed, the difference gave the weight of carbonaceous matter. The glass combustion tube, with a calcium chloride tube in the forward end, was heated to redness in the furnace and slowly cooled in a current of oxygen. When cool the calcium chloride tube was replaced by a weighed U tube containing dried calcium chloride, and a weighed potash bulb and drying tube (the latter protected by an additional drying tube to prevent its absorbing moisture from the outside air) were attached; the rear end of the tube was opened, the roll of oxidized copper wire withdrawn, the platinum boat pushed forward into the tube until it nearly touched the asbestos plug, and the roll of oxidized copper wire and the cork replaced as quickly as possible.

The forward end of the tube containing the roll of silver foil and the coarse copper oxide was first heated to redness (a current of oxygen passing through all the time), then the roll of oxidized copper wire and finally the boat, the heat being maintained until the carbonaceous matter was burned. The current of oxygen was replaced by one of air and the apparatus slowly cooled. When cold the calcium chloride tube and the potash bulb and drying tube were again weighed, the increase of weight in the former giving the water and that in the latter the carbon dioxide from the carbonaceous matter. The boat was carefully withdrawn and re-

turned to the test tube (which during the combustion had been kept in the desiccator) and the whole weighed as before. The loss of weight of course gave the amount of the volatile portion of the carbonaceous matter, and the increase of weight over that of the empty boat and the tube the amount of ash.

I expected of course to find the water, carbon and ash sum up to nearly 100 per cent., and was much surprised to find a deficiency of about 10 per cent. in my first analysis. I therefore repeated the operation several times with practically the same result.

The water varied only about 1.5 per cent. or from 20.50 per cent. to 22.00 per cent., while the carbon gradually decreased as the temperature and length of time of drying increased. When the carbonaceous matter was dried for about two hours at 95° to 100° C. I obtained 70 per cent. carbon, dried for 144 hours at 100° C. I obtained 64 per cent. carbon. Fearing some error in method or manipulation I then tried pure loaf-sugar in exactly the same way, and found

Carbon . . .	42.30
Water . . .	57.51
	99.81

This result was so satisfactory that I concluded I must look elsewhere for a reason for the deficiency in the carbonaceous matter; and it occurred to me that as steel contained nitrogen, that element might be found in the carbonaceous residue.

Careful determinations gave me nitrogen 0.45 per cent. I then thought that perhaps the carbon, at the instant of its separation, might take up chlorine from the copper chloride, as it takes up iodine and bromine when these elements are used in the decomposition of steel. A portion of the carbonaceous residue burned with pure lime gave me chlorine 2.59 per cent.

The only element left was oxygen. I therefore prepared a quantity of oxide of copper and made a direct determination of oxygen, following Stromeyer's[1] method, in sugar, when I obtained oxygen 51.47 and 51.42, theory 51.46.

As the carbon varied so much in the carbonaceous matter, it was necessary that the samples should be identically the same for the

[1] Ann. der Chem. und Phar. **117**, 247.

determinations of carbon and oxygen. Three small test tubes and platinum boats were therefore prepared, with a little wire rack to hold them, and three portions of carbonaceous matter weighed out as before.

After drying for several hours the rack was transferred to a desiccator, the tubes weighed, and while one boat was in the combustion tube I made an oxygen determination in the second portion and a chlorine determination in the third.

Two analyses resulted as follows:

	No. 1, dried 48 hours at 100° C.		No. 2, dried 144 hours at 100° C.	
Carbon	64.54	per cent.	64.30	per cent.
Water	21.03	" "	20.28	" "
Excess of O	8.01	" "	8.86	" "
Chlorine	3.76	" "	3.76	" "
Nitrogen	0.45	" "	0.45	" "
Ash	2.53	" "	2.45	" "
	100.32		100.10	

These results certainly differ very materially from those obtained by Schützenberger and Bourgeois; but as theirs were obtained by treating the iron with copper sulphate, I thought it worth while to examine the carbonaceous matter liberated by this reagent as well. I obtained,

	I.		II.	
Carbon	67.34	per cent.	67.17	per cent.
Water	22.83	"	22.50	"
Ash	2.15	"	2.08	"
	92.32		91.75	

Leaving out the chlorine, these left about the same deficiency that there was in the partial analyses of the carbonaceous matter liberated by the action of the double chloride of copper and ammonium on the steel.

Another portion of the carbonaceous matter liberated by the action of the double chloride of copper and ammonium was heated in a glass tube in a current of hydrogen. It lost 39.25 per cent. of its weight, of which only 12.54 per cent. was water. There was no appearance of oily or tarry matter, and the residue did not appear crystalline, and burned off readily in oxygen.

Heated in hydrogen, lost	39.25	per cent.
Residue contained carbon	57.84	"
" " ash	2.91	"
	100.00	

If the 20 or 22 per cent. of water found by combustion in oxygen existed as hydrate, one would naturally expect to find it given off by heating; and if the oxygen in excess of the amount necessary to form water were merely occluded, one would expect it to unite with the hydrogen, thus forming an additional amount of water. As neither of these things occurs, it seems reasonable to suppose that the elements carbon, hydrogen and oxygen are combined in some more intimate way than as a hydrate of carbon.

So much remains to be done, however, before the nature of this residue can be known that I do not even venture to give a probable formula for it, and can only hope that this may lead some one to enter a field that certainly, to me, looks very promising.

NEWPORT, R. I.

Contributions from the Chemical Laboratory of Harvard College.

XII.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.[1]

PARABROMBENZYL COMPOUNDS.

BY C. LORING JACKSON AND WOODBURY LOWERY.

Parabrombenzylalcohol ($C_6H_4BrCH_2OH$).—This substance was most easily prepared by boiling parabrombenzylbromide with water, in a flask with a return-cooler, for two or three days, until it no longer attacked the eyes. The reaction ran as follows:

$$C_6H_4BrCH_2Br + H_2O = C_6H_4BrCH_2OH + HBr.$$

The presence of the hydrobromic acid was established by treating the acid aqueous filtrate with argentic oxide, when argentic bromide was formed, and the solution became neutral. This method is analogous to that employed by Grimaux[2] for converting

[1] From the Proceedings of the American Academy. Communicated by the Authors.

[2] Grimaux, Comptes Rend. **70**, 1363; Ann. Chem. Pharm. **155**, 338.

tollylenebromide into tollyleneglycol, except that Grimaux heated the haloid compound with water at 170° to 180°, while we obtained the alcohol by boiling in a flask with a reverse-cooler. The alcohol was also obtained in the ordinary way by heating parabrombenzyl-acetate with aqueous ammonia in a sealed tube to 160°. In which-ever way prepared it was purified by crystallization from ligroin, and its composition established by the following combustion:

0.2298 gram of substance gave 0.3765 gram of CO_2 and 0.0789 gram of H_2O.

	Required for $C_7H_6Br.OH$.	Found.
Carbon	44.92	44.69
Hydrogen	3.74	3.84

Properties.—It forms long elastic transparent colorless flattened needles, with a brilliant pearly lustre and a disagreeable odor; its vapor does not attack the eyes. Melting-point, 77°. It burns with a luminous green-bordered flame, distils with steam although slowly, and is very slightly soluble in cold, more freely in boiling water, easily soluble in alcohol, ether, benzol, and carbonic disulphide.

Parabrombenzylcyanide ($C_6H_4BrCH_2CN$) was obtained by boiling parabrombenzylbromide with an alcoholic solution of potassic cyanide as long as potassic bromide was formed: on addition of water a yellow oil was precipitated, which deposited crystals after standing for some time, and finally solidified completely. The crystals were drained on filter-paper, and purified by crystallization from alcohol. Their composition was determined by the following volumetric nitrogen determination:

0.3565 gram substance gave 20 cc. nitrogen under a pressure of 742 mm. and a temperature of 9°.

	Required for C_7H_6BrCN.	Found.
Nitrogen	7.10	6.58

Properties.—The substance separates from the oil at first obtained, either in flat truncated octahedra with a marked basal cleavage belonging either to the tetragonal or orthorhombic system, and having a very strong resemblance to the crystals of ferrocyanide of potassium, or else in flat twins imitating in a very beautiful manner the architectural form of the quatrefoil. These crystals are yellowish white, but the substance is rendered colorless by crystallization from alcohol; it has a disagreeable odor, does not attack the eyes,

melts at 47°, burns with a luminous green bordered flame, and is insoluble in water, moderately soluble in cold, freely in hot alcohol, soluble in ether and glacial acetic acid, still more readily in carbonic disulphide and benzol; by boiling with alcoholic potassic hydrate or heating in a sealed tube with hydrochloric acid it is easily converted into parabromalphatoluic acid.

Parabromalphatoluic Acid ($C_6H_4BrCH_2COOH$).—This substance was most easily obtained by heating the cyanide with crude fuming hydrochloric acid to 100° in a sealed tube. On cooling, the liquid was found to be full of shining flattened needles of the acid, another portion of which had fused on the side of the tube; this method gave better results more neatly than the saponification with potassic hydrate; the acid was purified by recrystallization from boiling water, and its composition established by analyses of its silver and copper salts. (See below.)

Properties.—It crystallizes in white glistening flattened needles with but little odor, melts at 114°, sublimes above its melting-point in little plates, and burns with the usual luminous green-bordered flame. It is but slightly soluble in cold, freely in boiling water, and in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid. Ammonic and sodic hydrates dissolve it at once, forming the corresponding salts; it seems to decompose carbonates, but very slowly and imperfectly: potassic dichromate and dilute sulphuric acid convert it with some difficulty into parabrombenzoic acid.

In 1869, Br. Radziszewski[1] obtained a substance which he called parabromalphatoluylic acid, by the action of bromine in the cold upon alphatoluylic acid; he does not describe it fully, but only says that it crystallizes in prisms melting at 76°, and gives baric and calcic salts crystallizing in warts, and easily soluble in water and alcohol; by oxidizing it with potassic dichromate and dilute sulphuric acid he obtained nothing but parabrombenzoic acid melting at 251°. In the same operation another acid was formed containing bromine, which melted at 99°, and was not further examined.

The discrepancy between our results and those of Radziszewski has been shown by Bedson[2] recently to be due to the formation of both the ortho and para compounds when alphatoluic acid is treated with bromine. By converting the product into its barium salt Bedson has succeeded in isolating both the para and the ortho-

[1] Radziszewski, Ber. d. ch. G. 2, 207. [2] Journ. Lond. Chem. Soc. 1880, 1, 90.

bromalphatoluic acids, and finds that the former melts at 114°-115°, the latter at 103°-104°, in agreement with our results.

Ammonic parabromalphatoluate, obtained by dissolving the acid in ammonic hydrate, and driving off the excess of ammonia on the water-bath, crystallized in long curving groups of colorless needles very soluble in water.

Argentic parabromalphatoluate ($C_6H_4BrCH_2COOAg$) was precipitated by adding the ammonic salt to argentic nitrate, as a white curdy mass similar in appearance to chloride of silver; it was washed with cold water, and dried at 60°.

0.3106 gram of the salt dissolved in dilute nitric acid, and precipitated with hydrochloric acid, gave 0.1375 gram AgCl.

	Required for $C_7BrH_6CO_2Ag$.	Found.
Silver	33.57	33.33

It is almost insoluble in water, perhaps a little more soluble in hot than in cold, but could not be obtained crystallized; it is readily soluble in dilute nitric acid; blackens slightly by exposure to the light, and even at a temperature of 60°.

Cupric parabromalphatoluate, $Cu(C_6H_4BrCH_2COO)_2$, was precipitated as a flocculent bluish green solid, on mixing cupric sulphate with the ammonic salt.

0.3028 gram of the salt gave 0.05028 CuO.

	Required for $Cu(C_8H_6BrO_2)_2$.	Found.
Copper	12.90	13.24

It is insoluble in water, but soluble in dilute hydrochloric acid.

The *baric salt*, obtained by neutralizing a solution of the acid with baryta water and evaporating, formed white indistinctly crystalline crusts easily soluble in water.

The *calcic salt* obtained in a similar way, and also, although very slowly, from calcic carbonate and a solution of the acid, appeared in the form of white warts; which, under the microscope, were seen to be globular groups of sharp needles looking somewhat like a chestnut bur; it was easily soluble in water.

The behavior of a solution of ammonic parabromalphatoluate with solutions of the following salts was also observed:

Mercurous salts, a heavy flocculent white precipitate.

Mercuric salts, a slight white precipitate.

Plumbic salts, a heavy white precipitate, somewhat soluble in boiling water, and separating from this solution in crystalline flocks.

Ferric salts, a pale yellow amorphous precipitate, while chromic, aluminic, manganous, cobaltous, nickelous, zincic, and magnesic salts produced no precipitate.

Parabrombenzylsulphocyanate ($C_6H_4BrCH_2SCN$) was made by boiling the bromide with alcoholic potassic sulphocyanate and purified by crystallization from alcohol at low temperatures.

0.2318 gram of substance gave 0.2447 gram of $BaSO_4$.

0.3804 gram of substance gave 0.3125 gram of AgBr.

Calculated for $C_7H_6Br.SCN$.		Found.
Sulphur,	14.03	14.50
Bromine,	35.09	34.95

Properties.—White ribbons often 5 cm. long, made up of needles united laterally; it has a strong odor similar to that of benzylsulphocyanate; melts at 25°, and is soluble in alcohol.

Parabrombenzylamines. Parabrombenzylbromide acts on alcoholic ammonia in the cold, giving a mixture of the three amines, or their bromides, from which the pure compounds can be easily obtained by washing out the bromide of the primary amine with water, treating the residue with sodic hydrate, and separating the secondary from the tertiary by crystallization from alcohol.

The *primary amine*, set free from its bromide with sodic hydrate, is an oil, which can be distilled with steam, and is soluble in ether; it is rapidly converted into the carbonate by exposure to the air.

The *carbonate*, obtained by treating the free base with carbonic dioxide, consists of little white prisms arranged in radiating groups, which melt at 131°–133°, are soluble in water and alcohol, insoluble or nearly so in ether, benzol, and carbonic disulphide.

The *chloride*, made from the carbonate with hydrochloric acid, forms flattened needles melting with apparent decomposition at 260°, soluble in water and hot alcohol, but slightly soluble in cold alcohol, and essentially insoluble in ether, benzol, and carbonic disulphide.

The *chlorplatinate*, $(C_6H_4BrCH_2NH_2)_2PtCl_6$, made from the chloride, and purified by washing with water, gave the following result on analysis:

0.3020 gram of the salt gave 0.0755 gram of Pt.

Calculated for $(C_7H_6BrNH_2)_2PtCl_6$.		Found.
Platinum	25.16	25.00

It crystallizes in orange-brown plates, apparently of the monoclinic system, grouped in forms like frost, and is but slightly soluble in cold water, more so in hot, and in alcohol.

The *secondary amine*, $(C_6H_4BrCH_2)_2NH$, is left on evaporating its alcoholic solution as an oil, which solidifies on stirring, and can be obtained crystallized. It melts at 50°, and is very freely soluble in alcohol and ether.

The *chloride* is obtained in glistening rhombic scales, often pennately twinned, by adding strong hydrochloric acid to an alcoholic solution of the base; it melts at 283°, and is nearly insoluble in cold, somewhat more soluble in hot water or alcohol, insoluble in ether.

The *chlorplatinate*, $[(C_6H_4BrCH_2)_2NH_2]_2PtCl_6$, formed by adding chlorplatinic acid to an alcoholic solution of the free base, after being washed with alcohol and dried at 100°, gave the following result on analysis:

0.4716 gram of salt gave 0.0802 gram of Pt.

	Calculated for $[(C_7H_6Br)_2NH_2]_2PtCl_6$.	Found.
Platinum	17.58	17.01

It is a yellow powder, nearly insoluble in alcohol and water.

The *tertiary amine*, $(C_6H_4BrCH_2)_3N$, was purified by recrystallization from ether, or from ligroin; in either case a matted mass of needles looking like cotton was obtained, but the melting-point differed according to the solvent used, the crystals from ligroin showing the constant melting-point 92°, those from common ether the constant melting-point 76°–78°. Two recrystallizations from ligroin were enough to raise the melting-point of the crystals from ether to 92°, while the same number from ether lowered it again to 76°–78°. The following analyses, however, prove that the substance dried *in vacuo* has the composition of the tertiary amine, whichever solvent was used in its purification.

I. 0.3800 gram of the crystals from ligroin, m. pt. 92°, gave 0.6680 gram CO_2 and 0.1200 gram H_2O.

II. 0.2515 gram of the crystals from ether gave 0.4430 gram CO_2 and 0.0890 gram H_2O.

0.2020 gram of the crystals from ether gave 0.2175 gram AgBr.

0.1888 gram gave 0.2022 gram. AgBr.

	Calculated for $(C_7H_6Br)_3N$.	Found. I. (Ligroin.)	II. (Ether.)	
Carbon	48.09	47.93	48.03	
Hydrogen	3.44	3.51	3.93	
Bromine	45.81	45.82		45.56

Properties.—Fine white needles matted together into a woolly mass or forming circular radiated groups, insoluble in water, very slightly soluble in alcohol hot or cold, not freely in warm ether, but easily in hot ligroin, from which it crystallizes on cooling. In the preparation from alcoholic ammonia and parabrombenzylbromide it sometimes appears in needles 12 cm. long.

No definite chloride could be obtained even by precipitating the platinum as sulphide from the chlorplatinate, and washing with alcohol, as this gave only a viscous varnish.

Triparabrombenzylamine chlorplatinate $[(C_6H_4BrCH_2)_3NH]_2PtCl_6$, made by adding chlorplatinic acid to an ethereal solution of the free base, and purified by washing with water, alcohol, ether and ligroin, gave the following result on analysis:

0.3254 gram of the salt gave 0.0432 gram of Pt.

	Calculated for $[(C_7H_6Br)_3NH]_2PtCl_6$.	Found.
Platinum	13.51	13.28

Corn-yellow indistinct crystals, insoluble or nearly so in all the common solvents.

XIII.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

By C. Loring Jackson.

THE RELATIVE CHEMICAL ACTIVITY OF CERTAIN SUBSTITUTED BENZYL BROMIDES.

The following paper contains an account of some experiments undertaken to compare the ease with which bromine can be removed from the side-chains of the substituted benzylbromides described in the first paper of this series: in other words, an attempt to establish some relation between the structure of a molecule and its chemical activity. The differences in structure, which I have taken up, are of two sorts,—those depending on difference in the position of the same element, as in the three monobrombenzylbromides; and those depending on the presence of different but related elements in the same position, as in parachlor-, parabrom-, and paraiodbenzylbromide.

After a careful consideration of the reagents by which the side-chain bromine could be removed from these substances in a simple metathetical reaction, I decided that sodic acetate promised the best results, and, after many experiments, adopted a method, which consisted in treating equivalent amounts of the substituted benzyl-bromides, for the same length of time and under the same conditions, with an alcoholic solution of sodic acetate, and determining by volumetric analysis the amount of sodic bromide formed from each according to the following general reaction,—

$$C_6H_4XCH_2Br + NaC_2H_3O_2 = C_6H_4XCH_2C_2H_3O_2 + NaBr,$$

in which X stands for the halogen atom attached to the benzol ring. But even this reaction, although less full of sources of error than most of those available, is not so well adapted to work of this sort as I could wish; since the action takes place so rapidly that small differences in the time of two experiments produce comparatively large differences in their results. I have tried, therefore, to make the time occupied in starting and stopping the action as short as possible, and have reduced the duration of the addition of the sodic acetate solution, by which the reaction is started, to five seconds; but I have not been so successful in stopping the reaction promptly, as this was done by precipitating the organic matter with water, of which so large a quantity was needed that the average duration of the addition was fifteen seconds.

This method of stopping the reaction by means of water is not above criticism; for, although I consider of little or no weight the possible objection that the reaction may continue forming more sodic bromide after the addition of water, yet the presence of even a small amount of the substituted benzylbromide will cause a serious error in the determination of the sodic bromide,[1] and it is very hard to remove this completely by filtration; that it is possible, however, if sufficient care is used, appears from the following experiment.

A mixture of parabrombenzylbromide and parabrombenzylacetate was dissolved in a little alcohol, and, after precipitating with

[1] This point is illustrated by the following experiments: A little parabrombenzylbromide was dissolved in alcohol, and precipitated with water; 2.30 cc. of a standard solution of argentic nitrate were added, and the mixture allowed to stand fifteen minutes; on titrating for silver, it was found that 0.41 cc., corresponding to 0.0069 gram of $AgNO_3$, had been lost, while another similar sample which stood for one hour and twenty minutes lost 1.59 cc., corresponding to 0.026 gram of $AgNO_3$.

water and filtering, 4 cc. of a standard solution of argentic nitrate added, upon titrating the liquid 5.3 cc. of the standard solution of potassic sulphocyanate were found to be necessary, the theoretical quantity being 5.27 cc.

In selecting a solvent, it was necessary to find one which would dissolve all the substances entering into the reaction; since Berthelot and Pean de St. Gilles[1] have shown that, when two liquids which do not mix are used, the amount of action depends to a large extent on the size of the surface of contact; and therefore no constant results can be expected. I have confirmed these observations, while studying the action of water on the substituted benzylbromides, as will be described later in this paper. Under these circumstances, alcohol seemed to be the only solvent admissible; but its use introduced a new source of error, since it acts on the benzylbromides, forming the corresponding ethyl ethers and hydrobromic acid, as is shown by the following experiment.

Some parabrombenzylbromide was boiled with absolute alcohol for fifteen minutes. After removing the organic matter by precipitation with water and filtration, a precipitate was formed on the addition of argentic nitrate.

This defect was removed as completely as possible by taking pains that the benzylbromides should be in contact with the alcohol for the same length of time in each series of experiments. Then the results depended, in each case, on two reactions, viz.:

$$C_6H_4XCH_2Br + NaC_2H_3O_2 = C_6H_4XCH_2C_2H_3O_2 + NaBr$$
$$C_6H_4XCH_2Br + C_2H_5OH = C_6H_4XCH_2OC_2H_5 + HBr$$

but, as the time of each was the same in all the experiments of a series, the occurrence of the second did not materially affect the result, especially as the amount of substance entering into this second reaction was very small.

The adjustment of the amount of alcohol to be used was no easy matter, because sodic acetate and bromide are very sparingly soluble in absolute alcohol, and any considerable dilution interferes with the solubility of the benzylbromides; nor could the difficulty be removed by increasing to any great extent the amount of alcohol, as this would have increased the length of time necessary to stop the reaction.

[1] Ann. Chim. Phys. 3d ser. **66**, 46; **68**, 238.

More important than any of the sources of error yet mentioned is that proceeding from the differences in volatility of the benzyl-bromides with alcohol vapor, since this must alter the amount of substance capable of entering into the reaction in each case by the quantity of bromide volatilized with the alcohol in the upper part of the flask; and it is principally to this cause, which I could find no way of removing, that I am inclined to ascribe the considerable variations in my results.

This discussion of the defects in the process shows that no absolute agreement in the numbers obtained can be expected; but they agree nearly enough to establish certain interesting relations between the rates of decomposition of some of these compounds.

Comparison of the Three Monobrombenzylbromides.

One gram of each substance was weighed in a wide-mouthed flask, the cork of which was fitted with a return-condenser and a short wide tube closed with a cork for the addition of the reagents, 10 cc. of absolute alcohol were added, and the mixture heated for seven minutes in a boiling water-bath. After which, 25 cc. of a saturated solution of sodic acetate in 99 per cent. alcohol, at 60° to 70°, were introduced, and the flask heated for a definite time, varied in each series of experiments; care being taken that the water-bath boiled violently during the whole time, and that the three flasks to be compared were immersed to the same depth, and arranged symmetrically in the bath. The action was stopped by the addition of a large quantity of water, the flask being removed from the bath at the same time; and, after filtering out the organic matter, the quantity of sodic bromide formed by the reaction was determined by Volhard's[1] excellent method of titration with sulphocyanate.

The brombenzylbromides used were made in the way described in the first paper of this series, and purified with the utmost care.

The sodic acetate was prepared by drying the crystallized salt in an air-bath. It yielded on analysis the following result:

0.7720 gram of $NaC_2H_3O_2$ gave 0.6655 gram of Na_2SO_4.

	Calculated.	Found.
Sodium	28.05	27.93

The absolute alcohol did not turn anhydrous cupric sulphate blue, and neither it, nor the acidified solution of the sodic acetate, gave a precipitate with argentic nitrate.

[1] Ann. Chem. u. Pharm. **190**, 1.

The 25 cc. of the alcoholic solution of sodic acetate contained a little more than enough of the salt to decompose the one gram of brombenzylbromide used, since,—

10 cc. of this solution yielded on evaporation 0.136 gram of sodic acetate, and therefore,—

25 cc. contained	0.340 gram
Needed for 1 gram brombenzylbromide .	0.328 gram
Excess	0.012 gram

The 35 cc. of alcohol present were much more than sufficient to dissolve all the sodic bromide formed, as a rough determination showed that,—

35 cc. of absolute alcohol dissolve 0.627 gram NaBr.
1 gram brombenzylbromide yields 0.412 gram NaBr.

All the substances, therefore, were in solution throughout the experiment.

The accuracy of the method was tested by the following experiments, in each of which two portions of parabrombenzylbromide were compared:

I. Time, five minutes.

A. 1 gram parabrombenzylbromide lost 0.1164 gram Br.
B. " " " 0.1102 gram Br.

Difference . . . . . 0.0062 gram Br.

	Percentage of total side-chain bromine removed.	B in per cent. of A.
A.	36.39	100.0
B.	34.47	94.7
	1.92	5.3

II. Time, seven minutes.

A. 1 gram parabrombenzylbromide lost 0.1484 gram Br.
B. " " " 0.1446 gram Br.

Difference . . . . . 0.0038 gram Br.

	Percentage of total side-chain bromine removed.	B in per cent. of A.
A.	46.36	100.
B.	45.21	97.5
	1.15	2.5

From these results it appears that the method can be trusted within 0.0062 gram of bromine, or 5.3 per cent. when the largest number is taken as 100.[1]

The results of the experiments, comparing the rate of decomposition of the three monobrombenzylbromides, are given in the following table; the first column of which gives the time from the addition of the acetate till the reaction was stopped by dilution with water, while, in the other columns, under the name of each substance the amount of bromine removed is given,—first in grams, and second in percentages of the total amount of side-chain bromine.

TABLE I.

Time in minutes.	Parabrombenzylbromide.		Metabrombenzylbromide.		Orthobrombenzylbromide.	
	Bromine in grams.	Per cent. of total.	Bromine in grams.	Per cent. of total.	Bromine in grams.	Per cent. of total.
5	0.0855	26.73	0.0621	19.41	0.0533	16.65
10	0.1261	39.41	0.0968	30.25	0.0700	21.88
20	0.1752	54.75	0.1329	41.54	0.1015	31.72
30	0.1880	58.76	0.1517	47.43	0.1412	44.13

On representing the percentages of the total side-chain bromine removed by curves, in which horizontal distance represents time, vertical per cents, it is found that those given by the para and meta compounds are comparatively regular, but that the ortho curve is decidedly irregular. The same fact is brought out by the following table, in which the amount of bromine removed from the ortho and meta compounds in each experiment is given in percentages of the amount derived from the para compound in the same experiment.

TABLE II.

Time in minutes.	Para.	Meta.	Ortho.
5	100	73.	62.
10	100	77.	55.
20	100	76.	58.
30	100	81.	75.

[1] The results of these experiments cannot be compared with those given in Table I., because the quantity of alcohol used was not the same.

The differences between the relative amounts of bromine removed from the meta compound in the first three experiments, tabulated above, fall within the limit of error of the process, which amounts to over five per cent. when the numbers are given in this form; and, although the amount of bromine removed during thirty minutes is somewhat larger, the difference between this and the highest of the other numbers is only four per cent. It is probable, therefore, that the relative rate of decomposition for the para and meta compounds remains constant in the interval of time between five and thirty minutes; and that the slight increase in the numbers with the time in the experiments at 5, 20, and 30 minutes, is entirely accidental, although this point can be settled only by a new series of observations with a more accurate method. If this is assumed to be true, the mean of the numbers given in the meta column will represent the rate at which the metabrombenzylbromide is attacked, in comparison with that for the para compound taken as 100. This mean is 77; that is, about three-quarters as much bromine is removed from the meta as from the para compound in the same length of time.

The numbers given in the ortho column show much more serious deviations, the maximum difference amounting to twenty per cent.; but, as I observed that these numbers increased essentially with the time during which the specimen had stood exposed to the air of a desiccator, the experiments having been tried in the following order,—10 minutes, 55 per cent.; 5 minutes, 64 per cent.; 20 minutes, 58 per cent.; 30 minutes, 75 per cent.—I was led to the conclusion that the substance was undergoing decomposition, which afterwards was proved to be the case by the following analyses: I. made before, II. and III. after, the series of experiments.

I. 0.2375 gram of orthobrombenzylbromide gave, by the method of Carius, 0.3565 gram AgBr.

II. 0.2950 gram of substance gave 0.3705 gram AgBr.

III. 0.4100 gram of substance gave 0.5210 gram AgBr.

	Calculated for $C_7H_6Br_2$.	Found.		
		I.	II.	III.
Bromine	64.00	63.87	53.46	54.07[1]

The complete study of this decomposition must be postponed till a future paper. I can only say here, that no appreciable amount

[1] As these experiments were made before the orthobrombenzylbromide was obtained in the solid state, I had no criterion of its purity except the analysis.

of free hydrobromic acid could be detected in the substance analyzed above, and that I have often found crystals of orthobrombenzoic acid in specimens of orthobrombenzylbromide which had stood exposed to dry air for several months. Whatever may be the nature of the change, it is evident that the ortho numbers are of no value; and no attempt was made to correct them by new experiments, because such an unstable substance as the orthobrombenzylbromide is entirely unfit for work of this sort.

I will add a number of other comparisons, which were made by less accurate processes during the elaboration of the method. They are given as in Table II., the amount of bromine removed from the para compound being taken as 100 in each experiment, and the amounts from the meta and ortho compounds given in percentages of this. Either two or four grams of substance were taken in each experiment.

TABLE III.

Time in Minutes.	Para.	Meta.	Ortho.
22	100	78	54
22	100	73	52
23	100	78	54
21	100	—	48
Mean,	100	76	52

These numbers, entitled to very little consideration as independent experiments, confirm the preceding results from the meta compound, even more closely than could be expected when the large limit of error is remembered: and further, would seem to indicate that the rate for the ortho compound is about one-half that for the para, if it is assumed, as before, that the relative rate does not vary with the length of time during which the reaction has run; a result confirmed by the experiment made first in the preceding series, and therefore entitled to the most weight, which gave 55 per cent.

Berthelot and Pean de St. Gilles,[1] in their classic researches on etherification, found that after a certain time the water set free in the reaction prevented further formation of the ether; in other words, that there was a limit to etherification. Although it did not seem probable that there would be such a limit to this reaction,

[1] Ann. Chim. Phys. 3d ser. **68**, 225.

some experiments were tried to test the question, with the following results:—

I. Time somewhat more than two hours:

1 gram of parabrombenzylbromide lost 0.3203 gram of bromine.

1 gram of metabrombenzylbromide lost 0.2701 gram of bromine.

0.8200 gram of parachlorbenzylbromide lost 0.3082 gram of bromine.

To this may be added the following, in which the method was somewhat different; in II. common alcohol being used, and in III. the reaction taking place in a sealed tube, with dilute alcohol as the solvent.

II. Two portions of parabrombenzylbromide, 1 gram each, lost in twenty-five minutes 0.3113 gram and 0.3074 gram of bromine.

III. In thirty minutes 0.3046 gram and 0.3093 gram of bromine.

The results of these three experiments, calculated into percentages of the side-chain bromine, are given for the sake of comparison in the following table:

TABLE IV.

I.	II.	III.
Para. 100.1	Para. 97.3	Para. 95.3
Meta. 84.4	" 96.1	" 96.7
Chlor. 96.4		

Owing to the different conditions under which they were made these series of experiments are not comparable with each other, or with the series given in Tables I. and II., even I. not having been made under exactly the same conditions; they show, however, that there is no limit to the reaction in the case of the parabrombenzylbromide and probably none in the case of any of these substances.

Action of Water on the Monobrombenzylbromides.

Another entirely different method was also tried, which consisted in heating the substituted benzylbromides with water in sealed tubes, and determining the amount of hydrobromic acid formed by the reaction,—

$$C_6H_4BrCH_2Br + H_2O = C_6H_4BrCH_2OH + HBr.$$

For this purpose one gram of each substance was weighed in a tube about 14 cm. long and 2 cm. wide; 5 cc. of water were

added, and, after sealing, the tubes were put into a hot chloride of calcium bath, provided with an air-tight tin cover carrying a return-cooler, which thus was kept at a constant temperature throughout the process. After a definite time the tubes were removed, cooled as rapidly as possible with cold water, and the contents washed into a beaker, and titrated with a standard solution of baric hydrate. The following experiments were made with two portions of para-brombenzylbromide to test the process.

	Time in Hours.	Temperature.	Percentage of side-chain bromine removed. Portion *a*.	Portion *b*.
I.	2	132°–134°	16.05	13.3
II.	2½	110°–134°	17.8	16.3

	I.	II.
a	100	100
b	83	92

The marked want of agreement between these numbers is undoubtedly due to the fact that the mixture was not homogeneous, and therefore the differences in size of the surface of contact between the water and benzylbromide in the different tubes had a marked effect on the result.

In spite of the inaccuracy of the method, two experiments were carried through with the following results:

TABLE V.

TEMPERATURE 135°.

Time in hours.	Parabrombenzylbromide.		Metabrombenzylbromide.		Orthobrombenzylbromide.	
	Bromine in grams.	Per cent. of total.	Bromine in grams.	Per cent. of total.	Bromine in grams.	Per cent. of total.
6	0.1421	43.85			0.0763	23.55
6	0.1268	39.15	0.0969	29.9	0.0918	28.35

These results calculated into the form of Table II. become:

Para.	Meta.	Ortho.
100		54
100	76	72

The very high number for the ortho compound in the second experiment is probably due to a previous decomposition of the substance similar to that observed in the principal series of experi-

ments. The other results, as far as they go, confirm those obtained by the acetate method.

In the following table all the numbers thus far obtained are compared:

TABLE VI.

ACETATE METHOD.

Time.	Para.	Meta.	Ortho.
5′	100	72	64
10′	100	77	55
20′	100	76	58
30′	100	81	75
21′	100	—	48
22′	100	78	54
22′	100	73	52
23′	100	78	54
	WATER METHOD.		
6 hours	100		54
6 hours	100	76	72
Mean	100	76	59

A series of comparative experiments with parachlorbenzylbromide, parabrombenzylbromide and paraiodbenzylbromide was also made by the sodic acetate method, which indicated that they lose bromine at the same rate, when they are used in molecular proportions. I will give here, however, only the results from the last series of experiments, as in the others I did not succeed in overcoming some of the sources of error mentioned in the introduction wholly to my satisfaction. These results are given as in Table II.

Time in Minutes.	Parachlorbenzylbromide.	Parabrombenzylbromide.	Paraiodbenzylbromide
25	100	97	99

Summary.

The results of this investigation are,—1. The side-chain bromine is removed from the three monobrombenzylbromides approximately at the following rates:

Para.	Meta.	Ortho.
100	76	55 (?)
or 4	3	2 (?)

when the quantity removed is less than 60 per cent. of the whole.

2. From parachlor-, parabrom-, and paraiodbenzylbromide at essentially the same rate, if quantities proportional to their molecular weights are used.

All these results need confirmation by more accurate experiments, but, as Menschutkin in one of the papers[1] of his beautiful series on the rate of etherification (the first[2] of which was published a year after the appearance of a preliminary notice[3] of my work) has announced his intention of studying the effect of aromatic isomerism, and with his better chosen reaction and more delicate method will be able to do the work much more easily and accurately than I could, I have decided not to pursue the subject farther.

So far as I have been able to find, the only paper on this subject, as yet published, is one by Post and Mehrtens,[4] who describe a single attempt to make out the relative acidity of the three nitrophenols by treating weighed amounts of baric carbonate with solutions of the corresponding quantity of the three isomeres, and after one week determining the amount of baric carbonate dissolved. In this way they got results which calculated in percentages of the amount from the para compound become:

Para. m. pt. 115°.	Meta. m. pt. 96°.	Ortho. m. pt. 45°.
100	57	93

and, therefore, agree with mine neither in order nor ratio.

AN ABSTRACT OF THE RESULTS OBTAINED IN A RECALCULATION OF THE ATOMIC WEIGHTS.

By F. W. Clarke.

During the past three years I have been engaged upon a recalculation of all the atomic weight determinations which have been published from the time of Berzelius' earlier investigations down to the present date. My purpose has been to reduce all similar series of experiments to common standards; to calculate the probable error of each series; to combine the results into general means; and then to deduce the atomic weights in such a way that each

[1] Ann. Chem. Pharm. **197**, 225.
[2] Ber. d. ch. G. **10**, 1728.
[3] Ber. d. ch. G. **9**, 931.
[4] Ber. d. ch. G. **8**, 1549.

value should represent a fair average of all the trustworthy estimations. In other words, I have sought to bring together all the vast number of scattered details, and to derive from them a more consistent table of atomic weights than has hitherto been found in chemical literature. My complete work will appear in due time as a separate volume; my present intention is to give merely a summary of my methods, and my conclusions.

Taking hydrogen as unity, I necessarily began with the ratio between it and oxygen. This ratio has been determined accurately in only two ways: First, by the synthesis of water over copper oxide, and secondly, from the relative density of the two gases. Ignoring earlier inexact experiments, we may consider only the data furnished by Dumas, by Erdmann and Marchand, and by Regnault. From Dumas' nineteen syntheses of water, we get for oxygen values varying from O=15.892 to O=16.024. The mean of all is 15.9607, with a probable error of ± .007. Erdmann and Marchand give eight results, which average O=15.9733; ± .0113. The general mean from both investigations is

$$O=15.9642;\ \pm .006.$$

The density of hydrogen, referred to air as unity, was determined by Regnault in three experiments. The mean was .069263; ± .000019. For oxygen four determinations were made by Regnault, and one of them was rejected. The three remaining figures give a density of 1.105633; ± .000008. The ratio between these two density estimations gives an atomic weight of

$$O=15.9628;\ \pm .0044.$$

Combining this with the value found from the synthesis of water, we get a general mean of

$$O=15.9633;\ \pm .0035.$$

This is the most probable value which can be deduced from the published data; and it forms the corner-stone upon which our entire system of atomic weights must rest. I need not discuss here the methods employed in the calculation of probable errors, for they are given in all treatises upon least squares. Suffice it to say that I assign no arbitrary weights to the values under examination. Each series of experiments receives the weight to which the probable error of its mean entitles it.

Having found a value for oxygen, I next discussed in a group the atomic weights of the elements chlorine, bromine, iodine, silver, potassium, sodium and sulphur. The data to be considered were determined by Berzelius, Penny, Pelouze, Marignac, Maumené, Gerhardt, Millon, Struve, Svanberg and Struve, Turner, Dumas, Cooke, and Stas; and represented twenty distinct ratios. For example, one of the most important ratios was that between potassium chloride and potassium chlorate; for which there were nine series of determinations. The mean of each series was calculated, together with its probable error, and then all nine means were combined into one general mean. Thus all the available data were reduced to the twenty compact ratios above referred to. Two of these may be cited to illustrate the methods of calculation.

1. Percentage of O in $KClO_3$, 39.154; ± .0004.
2. Ag : KCl : : 100 : 69.1032; ± .0002.

From the first of these ratios the molecular weight of KCl is easily calculated by the usual proportion, 39.154 : 60.846 : : O_3 : x. Using the value for oxygen previously found, x, or KCl, becomes 74.4217; and as the probable errors are known for the three known terms of the proportion, we easily deduce that of the fourth term, and write

$$KCl = 74.4217 ; \pm .0164.$$

Here the probable error is a function of the probable errors of the experiments upon potassium chlorate, and the probable error of the atomic weight of oxygen. We may now use this value for KCl in connection with the second of the ratios above cited, and deduce for the atomic weight of silver the figure

$$Ag = 107.696 ; \pm .024.$$

In every proportion used there are known probable errors for three terms, and they are involved in the probable error of the fourth term. From the twenty ratios above referred to, eight entirely independent values for the atomic weight of silver can be found. Each value has a definitely ascertained probable error, and each receives the weight which that error indicates. The general mean of all is

$$Ag = 107.675 ; \pm .0096.$$

This is the final result from the discussion of over two hundred experiments; and it gives us the key to the atomic weights of the

other elements in the group under consideration. These are as follows, when O=15.9633; ± .0035.

Cl = 35.370; ± .014
Br = 79.768; ± .019
I = 126.557; ± .022
K = 39.019; ± .012
Na = 22.998; ± .011
S = 31.984; ± .012

The values which Stas assigns to these elements are all based upon the standard of O=16. If we adapt the above figures to the same standard, we may compare them side by side with those of Stas. As the latter chemist also determined the atomic weights of nitrogen, lithium and lead, I will include the values found in this recalculation for these substances also.

ATOMIC WEIGHTS WITH O=16.

	New Values.	Stas' Values.	Difference.
Ag	107.923	107.930	— .007
Cl	35.451	35.457	— .006
Br	79.951	79.952	— .001
I	126.848	126.850	— .002
Na	23.051	23.043	+ .009
K	39.109	39.137	— .028
S	32.058	32.074	— .016
N	14.029	14.044	— .015
Li	7.0235	7.022	+ .0015
Pb	206.946	206.926	+ .020

The magnificent accuracy of Stas' manipulations could hardly receive more striking confirmation than is afforded by these figures.

The atomic weights of the remaining elements I give below, in the order of their calculation. I also give the authorities whose experiments are combined in the values presented. Elaborate details there is of course no room for; they must be sought in the complete monograph when the latter is published.

Nitrogen. Data by Regnault, Pelouze, Marignac, Turner, Penny, and Stas. General mean of all, N=14.0210; ± .0035. This value involves the values previously found for O, K, Na, Ag and Cl.

Carbon. Data by Liebig and Redtenbacher, Maumené, Dumas and Stas, Erdmann and Marchand, and Stas. General mean of all, C=12.0021; ± .0019. Rejecting the series by Liebig and Redtenbacher and by Maumené, which involve constant errors, we get from the remaining series a value of C=11.9736; ± .0028. If O=16 this becomes C=12.0011. The ratio between oxygen and carbon therefore is a ratio between two whole numbers, 16 and 12.

Barium. Determined by Berzelius, Turner, Struve, Pelouze, Marignac, Dumas, and Stas. General mean, Ba=136.763; ± .031. If O=16, Ba=137.007.

Strontium. Data by Pelouze, Dumas, and Marignac. General mean, Sr=87.374; ± .032.

Calcium. Experiments by Berzelius, Erdmann and Marchand, and Dumas. Ca=39.990; ± .010. The best single result by Erdmann and Marchand gives Ca=39.905; or, if O=16, Ca=39.997.

Lead. Berzelius, Turner, Marignac, Dumas, Anderson, and Stas. Some data were rejected. The final most probable value is Pb=206.471; ± .021.

Fluorine. Berzelius, Louyet, Dumas, and DeLuca. General mean, F=18.984; ± .007.

Phosphorus. The only good determinations for this element are those by Schrötter and by Dumas. General mean of both series, P=30.958; ± .007.

Boron. Berzelius, Laurent, Dumas and Deville. In mean, B=10.941; ± .023. Not well determined.

Silicon. Pelouze, Dumas, and Schiel. Si=28.195; ± .031 This constant needs thorough experimental revision.

Lithium. Mallet, Diehl, Troost, and Stas. General mean, Li=7.0073; ± .007.

Rubidium. Bunsen, Piccard, Godeffroy. Rb=85.251; ± .0045.

Caesium. Johnson and Allen, Bunsen, and Godeffroy. Cs=132.583; ± .024.

Thallium. Although I have recalculated the results obtained by Lamy, Hebberling, and Werther, I need consider here only the experiments of Crookes. His weighings, calculated with the values for O and N given above, make Tl=203.715; ± .037. Crookes himself, using the value NO_3=61.889, found Tl=203.642, and regards his results as evidence against Prout's hypothesis. His experiments, however, really fix only the ratio between NO_3 and

Tl. If $NO_3=62$, then Tl=204.008. That is, the ratio which Crookes has rigorously established is a ratio between two whole numbers, and is confirmatory of Prout's idea.

Glucinum. The results of Awdejew, Klatzo, Weeren, and Debray, have high probable errors, and practically vanish from the mean when combined with those of Nilson and Pettersson. The weighings published by the latter chemists give me Gl=9.085; ± .0055; or Gl=13.628; ± .008; according to whether the oxide is GlO or Gl_2O_3.

Magnesium. Scheerer, Svanberg and Nordenfeldt, Bahr, Jacquelain, Marchand and Scheerer, and Dumas. General mean of all, Mg=24.103; ± .004. Some of the series are vitiated by constant errors. The best value is to be deduced from Marchand and Scheerer's work alone, and is Mg=23.959; ± .005.

Zinc. Jacquelain, Favre, and Axel Erdmann. General mean, Zn=65.557; ± .011. Erdmann's results alone, however, give a more probable value (considered chemically) of Zn = 64.9045; ± .019.

Cadmium. Von Hauer, Lenssen, and Dumas. General mean, Cd=111.770; ± .030.

Mercury. Part of Turner's data are to be considered, together with results by Erdmann and Marchand, Millon, and Svanberg. General mean, Hg=199.712; ± .042. New determinations are much needed.

Chromium. Peligot's work was not available for discussion. The data studied were by Berlin, Moberg, Lefort, Wildenstein, Kessler, and Siewert. General mean from all, Cr=52.453; ± .015. Berlin's work, considered by itself, gives Cr=52.389; ± .019. Siewert's results give Cr=52.009; ± .025. I regard the last value as freest from constant errors, and use it in subsequent calculations.

Manganese. Turner, Berzelius, Dumas, v. Hauer, Schneider, and Rawack. General mean, Mn=54.128; ± .011. Schneider's and Rawack's results give a better value of Mn=53.906; ± .012.

Iron. Berzelius, Svanberg and Norlin, Erdmann and Marchand, Maumené, Rivot, and Dumas. General mean, Fe=55.913; ± .012.

Copper. Berzelius, Erdmann and Marchand, Millon and Commaille, and Hampe. Cu=63.173; ± .011.

Molybdenum. Debray, Dumas, Rammelsberg, and analyses by Liechti and Kemp. Mo=95.527; ± .051.

Tungsten. Berzelius, Schneider, Marchand, v. Borch, Dumas, Bernoulli, Persoz, Roscoe, Scheibler, and Zettnow. General mean of all, W=183.610; ± .032.

Uranium. Peligot, Ebelmen, and Wertheim. General mean, U=238.481; ± .082.

Aluminum. Berzelius, Tissier, Isnard, Dumas, Terreil, and Mallet. General mean, Al=27.0092; ± .0028. All the data except Mallet's might be rejected without essentially affecting this value.

Gold. Berzelius, and Levol. Au=196.155; ± .095. A thorough redetermination is much needed.

Nickel. Several early series for nickel and cobalt were rejected. The data taken were by Schneider, Dumas, Russell, Sommaruga, Winkler, and Lee. General mean, Ni=58.547; ± .009. I attach more importance to the concordant results of Schneider, Sommaruga, and Lee, whose figures give a general mean of Ni=57.928; ± .022, Lee's investigation was of all the least susceptible to constant errors.

Cobalt. Schneider, Dumas, Russell, Sommaruga, Winkler, Weselsky, and Lee. Co=58.887; ± .008.

Selenium. Berzelius, Sacc, Erdmann and Marchand, Dumas, and Ekman and Pettersson. Se=78.797; ± .011.

Tellurium. Berzelius, v. Hauer, and Wills. General mean, Te=127.960; ± .034. The results of v. Hauer and Wills upon K_2TeBr_6 give Te=127.170; ±.173. Wills' minimum figures give me Te=126.07. In all of these results certain constant errors are possible; so that the question raised by Mendelejeff as to whether tellurium is above or below iodine, cannot be regarded as settled.

Vanadium. Roscoe's weighings, recalculated with the new values for O, Ag, and Cl, give V=51.256; ± .024.

Arsenic. Pelouze, Dumas, Wallace, and Kessler. General mean, As=74.918; ± .016. Wallace's analyses of $AsBr_3$ were made to establish the atomic weight of bromine, but they serve a better purpose here.

Antimony. For this element there have been the two rival figures 120 and 122. The general mean from data by Kessler, Dumas, and Dexter, is Sb=122.092; ± .035. The general mean from the experiments of Schneider and of Cooke is Sb=119.955; ± .036. In view of the recent discussions upon the subject, we may regard the lower figure as established.

Bismuth. General mean from Schneider's experiments, Bi= 207.523; ± .082. If O=16, this becomes 208.001. All of Dumas' results on bismuth chloride give a mean of Bi=210.464; the figures which he considers best give Bi=209.78. Schneider's work is probably nearest correct, his method being less liable to constant errors than that of Dumas.

Tin. Berzelius, Mulder and Vlaanderen, Dumas, and Vlaanderen. General mean, Sn=117.698; ± .040.

Titanium. Rose's weighings give Ti=48.710; ± .105. Mosander's figures give Ti=47.045. Pierre's give Ti=49.889; ± .096; and Demoly's, Ti=52.191; ± .153. A general mean of the results of Pierre, Rose, and Demoly is 49.846; ± .064. Mosander's work must be rejected, for want of sufficient details. An experimental revision is wanted.

Zirconium. From Berzelius' figures Zr=89.255; ± .039. From Marignac's data Zr=90.328; ± .113. The general mean of both sets is Zr=89.367; ± .037. New determinations are evidently needed.

Thorium. Berzelius, Chydenius, Berlin, Delafontaine, Hermann, and Cleve. General mean, Th=233.414; ± .073.

Gallium. From Boisbandran's results, in mean, Ga=68.854.

Indium. Reich and Richter, Winkler, and Bunsen. General mean, In=113.398; ± .047.

Cerium. Beringer, Hermann, Marignac, Bunsen and Jegel, Rammelsberg, Wolf, Wing, and Buehrig. General mean of all, Ce=140.424; ± .017. Buehrig's analyses of the oxalate give Ce=141.198; ± .020. The figures by Wolf and by Wing give Ce=137.724. Wolf and Wing had a *white* ceroso-ceric oxide, and Wolf suspects the ordinary yellowish compound to contain a fourth metal of the cerium group. Buehrig's work is the best, but the possible presence of a fourth metal is not considered by this chemist. Therefore new experiments are needed.

Lanthanum. Hermann, Rammelsberg, Marignac, Czudnowicz, Holzmann, Zschiesche, Erk, and Cleve. General mean, La= 138.526; ± .030.

Didymium. Marignac, Hermann, Zschiesche, Erk, and Cleve. General mean, Di=144.573; ± .031. Cleve's work alone, which is doubtless the best, gives Di=146.804.

Scandium. Nilson's results, recalculated, give Sc=43.980; ± .015.

Yttrium. Popp, Delafontaine, Bahr and Bunsen, and Cleve. General mean, Yt=97.616. Excluding Popp's work as worthless, the general mean becomes Yt=89.816; ± .067.

Ytterbium. Nilson. Yb=172.761; ± .038.

Erbium. For this metal the most probable results are those of Cleve, which give, recalculated, Er=165.891. Previous workers undoubtedly studied material rich in ytterbium and other metals of the group.

For terbium, samarium, phillipium, decipium, thulium, etc., there are no satisfactory data. Cleve gives 170.7 for thulium, while Delafontaine puts Ph=123 to 125, and Dp=171. These figures assume that all the earths of the group are sesquioxides.

Columbium.[1] Marignac's results give approximately Cb=94. Blomstrand regards 95 as the most probable value. New estimations are needed.

Tantalum. All of Marignac's figures give a general mean of Ta=182.144; ± .166. Probably 182 may be safely used as the true value.

Platinum. By a recalculation of the results lately published by Seubert, I get Pt=194.415; ± .049.

Osmium. Berzelius' figures give me Os=198.494.

Iridium. The general mean calculated from Seubert's weighings is Ir=192.651; ± .033.

Palladium. Berzelius' last results are the only ones worth considering. They give Pd=105.737.

Rhodium. Data by Berzelius. Rh=104.055.

Ruthenium. A single analysis of potassium rutheniochloride by Claus gives Rh=104.217. Plainly, the values for Ru, Rh, Pd, and Os need scrupulous redetermination.

Conclusions.

A careful scrutiny of all the data upon which the foregoing atomic weight calculations depend, will reveal various sources of error. Of course, each series of results must be considered by itself, and weighed on its own merits; but a few general errors are important enough to warrant mention here.

[1] This name has priority over the generally accepted "niobium," and therefore is entitled to preference.

First, every value after oxygen, with one or two partial exceptions, involves whatever error may attach to the atomic weight of oxygen. If the latter is 16, instead of 15.9633, this error in some instances becomes multiplied to a serious extent, as a glance at the tabulated results will show. Other similar errors are repeated continually. The value assigned to any element is necessarily affected by whatever errors may attach to the atomic weights of those other elements through whose medium it is referred to the standard, hydrogen.

Secondly, confusion arises from the fact that many of the weighings under discussion were not reduced to the standard of a vacuum, while others had been subjected to such a correction. The errors thus introduced into the calculations are small, but still they cannot be lost sight of.

Another set of errors of unknown magnitude are produced as follows. Many series of experiments, notably in the work of Stas, Marignac, and other eminent investigators, involve the titration of chlorides, bromides, or iodides with solutions containing known weights of metallic silver. But Dumas has lately shown that silver purified after the usual methods occludes weighable quantities of oxygen. In other words, the silver hitherto employed in atomic weight investigations has not been pure silver. One exception is found in Mallet's research upon aluminum. Since the atomic weights of nearly all the elements depend directly or indirectly upon silver, this source of error becomes of the greatest importance. Analogous errors may possibly occur with metals other than silver, and should be carefully looked for. For example, the atomic weights of both copper and oxygen depend upon the reduction of copper oxide in hydrogen. If the residual copper, which is weighed, occludes any hydrogen, then the atomic weight of copper will come out too high, and that of oxygen a trifle too low. Such an error might account for the difference between 15.9633 and 16 in the case of oxygen.

In connection with the data discussed in this investigation it is perhaps worth while to consider the bearing of the results upon Prout's famous hypothesis. In order to simplify matters I tabulate the new atomic weight values in two columns; one containing numbers referred to hydrogen as unity, the other with figures comparable with oxygen as equal to sixteen.

Table of Atomic Weights.

	H=1.	O=16.		H=1.	O=16.
Hydrogen,	1.0000	1.0023	Sodium,	22.998	23.051
Fluorine,	18.984	19.027	Potassium,	39.019	39.109
Chlorine,	35.370	35.451	Rubidium,	85.251	85.529
Bromine,	79.768	79.951	Caesium,	132.583	132.918
Iodine,	126.557	126.848	Silver,	107.675	107.923
Lithium,	7.0073	7.0235	Thallium	203.715	204.183
Glucinum,	9.085	9.106	Phosphorus,	30.958	31.029
Magnesium,	23.959	24.014	Vanadium,	51.256	51.373
Zinc,	64.905	65.054	Arsenic	74.918	75.090
Cadmium,	111.770	112.027	Antimony,	119.955	120.231
Mercury,	199.712	200.171	Bismuth,	207 523	208.001
Calcium,	39.990	40.082	Columbium,	Ab't 94.	Ab't 94.
Strontium,	87.374	87.575	Tantalum,	182.144	182.562
Barium,	136.763	137.007	Scandium,	43.980	44.081
Lead,	206.471	206.946	Yttrium,	89.816	90.023
Oxygen,	15.9633	16,0000	Erbium,	165.891	166.273
Sulphur,	31.984	32.074	Ytterbium,	172.761	173.158
Selenium,	78.797	78.978	Cerium,	140.424	140.747
Tellurium,	127.960	128.254	Lanthanum,	138.526	138.844
Chromium,	52.009	52.129	Didymium,	144.573	144.906
Molybdenum,	95.527	95.747	Carbon,	11.9736	12.0011
Tungsten,	183.610	184.032	Silicon,	28.195	28.260
Uranium,	238.482	239.030	Titanium,	49.846	49.961
Manganese,	53.906	54.029	Zirconium,	89.367	89.573
Iron,	55.913	56.042	Tin,	117.698	117.968
Nickel,	57.928	58.062	Thorium,	233.414	233.951
Cobalt,	58.887	59.023	Platinum,	194.415	194.867
Copper,	63.173	63.318	Iridium,	192.651	193.094
Boron,	10.941	10.966	Osmium,	198.494	198.951
Aluminum,	27.009	27.075	Palladium,	105.737	105.981
Gallium,	68.854	68.963	Rhodium,	104.055	104.285
Indium,	113.398	113.659	Ruthenium,	104.217	104.457
Nitrogen,	14.021	14.029	Gold,	196.155	196.606

Here we have sixty-six elements, or rejecting columbium as too vaguely determined, sixty-five. Such elements as phillipium, decipium, thulium, samarium, etc., are not yet sufficiently well known to be considered in this connection.

In his recent superb investigation of the atomic weight of aluminum, Mallet makes substantially the following argument in favor of Prout's hypothesis. Considering the atomic weights of eighteen elements only as well determined, he finds that ten of them have values varying less than 0.1 from whole numbers. In other words, these ten elements have atomic weights varying from even multiples of that of hydrogen by insignificant amounts. What is the probability that this agreement with Prout's hypothesis in ten cases out of eighteen is purely accidental, as those hold who agree with the views of Stas? Working this problem out he finds the probability of mere coincidence to be 1 : 1097.8, and he concludes that Prout's hypothesis is still worthy of careful consideration.

Applying Mallet's reasoning to the table of atomic weights now before us, we find that in the first column, when H=1, twenty-five out of sixty-five elements have atomic weights falling within one-

tenth of a unit of whole numbers. But many of the figures which fall outside this limit of variation involve the variation of oxygen multiplied many times over. We must, therefore, study the second column which assumes O=16. Here we have thirty-nine elements falling within the limit of variation assigned by Mallet, and twenty-six falling without. The latter are chlorine, iodine, potassium, thallium, glucinum, mercury, strontium, tellurium, chromium, molybdenum, rubidium, copper, indium, vanadium, antimony, tantalum, erbium, ytterbium, cerium, lanthanum, silicon, zirconium, platinum, rhodium, ruthenium, and gold. Of these, chlorine, rubidium and strontium agree closely with half multiples of hydrogen; while tellurium, molybdenum, indium, tantalum, erbium, cerium, silicon, zirconium, lanthanum, rhodium and ruthenium may be dismissed from consideration as not sufficiently well determined to bear upon the problem before us. The exceptions in the cases of potassium, iodine, thallium, glucinum, mercury, chromium, vanadium, antimony, ytterbium, platinum and gold, remain to be considered.

For potassium and iodine, we must remember that both of these elements involve the constant error due to the occlusion of oxygen by silver. This error is probably great enough to throw the values for both elements outside the limit of variation above assigned. For thallium, it has already been shown that when its atomic weight is calculated with $NO_3=62$, Crookes' data give Tl=204.008. The atomic weights of glucinum and ytterbium, as given in the tables, are calculated from analyses of the sulphates. If $SO_3=80$, then Gl=9.096, and Yb=173.016. Both fall within, and one *narrowly* within the limit of one-tenth of a unit variation. In the case of platinum I need only say that Seubert's figures give values ranging both above and below the even number 195; while as for antimony, although the general mean is Sb=120.231, Cooke's analyses of the bromide, reckoned with Br=80, give almost exactly 120 for the value. For mercury, chromium, vanadium and gold, new determinations are desirable.

Enough has been said to show that none of the apparent exceptions to Prout's hypothesis are absolutely inexplicable. As the figures actually stand, thirty-nine out of sixty-five elements vary less than a tenth of a unit each from even multiples of the atomic weight of hydrogen. Of the remaining twenty-six, three conform to half multiples, three more are legitimately recalculable so as to

fall within bounds, and eleven have been so defectively determined that the assigned values can carry scarcely any weight. The remaining nine are still subject to slight revision. In short, the many agreements, which include three-fourths of the *well* determined atomic weights, render Prout's hypothesis very highly probable. It is more likely that the seeming exceptions are due to undetected constant errors, than that the great number of coincidences should be accidental. The mathematical probability in favor of Prout's hypothesis I have not yet calculated, but a glance at Mallet's figures will show that it must be enormous.

As I said at the beginning, this paper is but a summary of methods and conclusions. Within its scope, elaborate discussions would not be admissible. I hope that my complete memoir will soon be published; and it is my intention to discuss, in an appendix to it, both the bearing of the results upon Prout's hypothesis, and the distribution of the variations therefrom. I ought to say that at the beginning of my investigation I was strongly prejudiced against Prout's hypothesis, and fully believed that it had been forever overthrown. My results have forced me to give it very respectful consideration.

METHOD FOR ACCURATE AND RAPID ANALYSES OF AIR.

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I have made a series of daily analyses in duplicate of air collected at this place for six months beginning with January 1, 1880, and one for six months and twenty days, beginning October 1, 1880. The samples of air were collected in bottles with well fitting glass stoppers. A few drops of solution of potassium hydrate being put into the bottle, this was set in the open air, and the air in the bottle displaced by sufficient aspiration, the observer keeping at a little distance to the leeward side. The stopper was then put in place and wet with the potassium hydrate by inverting the bottle and turning the stopper. Experiment showed that it was possible to keep samples for many days in this way with the certainty that they remained unchanged.

A mercury pump was used to withdraw the sample from the bottle. A rubber stopper was used to make the needed connection with the pump. Experiment showed that this rubber in contact with the alkaline solution does not absorb more than a hundredth per cent. of oxygen from the air in the bottle in twenty times the period during which it was in contact with the air used in the analysis. The pump discharged the air into a jar standing over mercury in the laboratory trough of the apparatus for analysis.

This jar being lowered, together with the cistern, over the recurved capillary end of the eudiometer tube, a certain quantity of air was taken into this tube. This quantity was measured approximately by using a journeyman pressure tube having a small bore. The quantity used was almost always the same, and occupied from 470 to 475 millimetres in length of the eudiometer tube, when the pressure on it was that of a column of mercury of this same length.

This quantity was then measured accurately with the standard pressure tube. This had a Jolly point in the vacuum at the level of the zero of the graduation on the eudiometer tube, which zero was at the top of the tube. The level of the mercury in the standard pressure tube being never permitted to vary more than a fraction of a millimetre, its vacuum was found to remain constant and unimpaired. When the mercury in it had been put in connection with the mercury in the eudiometer, and its upper level had been brought to the Jolly point by the use of a fine adjustment, the level of the mercury in the eudiometer was read with a microscope magnifying fifty diameters, and provided with an eye-piece micrometer. By this arrangement, when everything was prepared, it was possible to verify the contact at the Jolly point, to read the thermometer to the hundredth of a degree, and to read the level of the mercury in the eudiometer, in less than ten seconds. Uncertainty as to the actual temperature at the instant of final reading was in this way mostly avoided. This reading microscope is carried on a vertical cylinder which is solidly attached to the firm iron tripod which supports the whole apparatus. On this cylinder the mounting of the microscope can be clamped at the required height. The microscope is then made to give distinct vision of the graduation on the surface of the eudiometer. This graduation consists of lines not more than the eight thousandth of an inch wide, cut with a diamond. No errors exist amounting to the hundredth of a millimetre in the parts of the

graduation which have been used in these analyses. When distinct vision is obtained of the graduation, a fine adjustment moves the microscope vertically till the terminal lines of the eye-piece micrometer coincide with two lines of the graduation on the eudiometer. If now the horizontal focusing movement carries the microscope forward about half an inch towards the eudiometer, the microscope will give distinct vision of the meniscus in the tube, and its level can be read by the divisions of the eye-piece micrometer, which represent the divisions on the surface of the tube carried forward optically into its interior. It would be easy to show how far the use of such an arrangement is superior to that of a cathetometer for the purpose in hand, in accuracy, in rapidity, and in simplicity of reduction for expansion of the scale.

The measured quantity of air was next transferred to a jar standing over mercury in the laboratory trough.

A quantity of hydrogen amounting to about sixty-three per cent. of the air taken was next measured approximately, and added to the air in the jar. This amount was always the same, so that any errors which were a function of the quantity of hydrogen should be constant in amount, and should not therefore affect the *differences* of the analyses. Sixty-three per cent. was used in order that the last and first readings of volume might be made with the same position of the reading microscope.

After the air and hydrogen had had time thoroughly to mix, they were transferred back to the eudiometer, measured, expanded, exploded, and again measured. The expansion was always the same. In the transfers mentioned there is absolutely no possibility of loss or of admixture by leakage except by gross carelessness. The only place where leakage could take place is the stop-cock at the top of the eudiometer. This stop-cock was specially made for this place, and has not yet been found to leak, though it has been tested for ten minutes against an internal vacuum before or after each analysis.

Two coincident readings were obtained for each measurement, though the result was always calculated from the last reading. To secure accurate determinations of temperature, the eudiometer and pressure tubes are enclosed in a box with plate-glass front and back, containing about ten litres of distilled water. This is vigorously stirred, except at the instant of reading the microscope, by means of a current of air from a condensing pump driven by power. I

have had no difficulty in getting the required two coincident readings in half a minute when the thermometer was rising; but when the thermometer is falling, the difficulty in getting a reading of the thermometer which shall really represent the temperature is enough to make work very vexatious, for an error of a hundredth of a degree in the difference of temperature at two measurements in the same analysis is close upon the limit of allowance.

Great care has been taken to obtain hydrogen of sufficient purity. In the early analyses, a Bunsen's decomposing cell of the common form was used. It then often happened that the analysis made with the first hydrogen obtained after an interval of rest would give results showing a deficiency of oxygen of about a hundredth of one per cent. Often analyses had to be rejected, until the cell was freed from compounds of hydrogen with zinc or carbon, which had been produced by local action at the surface of the zinc. Finally, a cell was constructed which could be every morning connected with the air-pump and exhausted of hydrogen, so as to remove these compounds of hydrogen with zinc or carbon, whether they had risen through the liquid, or were still adherent to the zinc plate or dissolved in the dilute acid. The cell had a mercury stop-cock which interposed a barometric column against the leakage of air into the cell; but for additional security, the hydrogen coming from it passed through several inches of active platinum black. In this way I have now secured a supply of hydrogen which probably never occasions a difference of a five hundredth of one per cent. in two analyses of the same sample. Experiment shows that hydrogen may safely be left standing over mercury in a *clean* bell-glass for a long time. I have left two samples for eleven weeks, which samples then were used in a duplicate analysis of a sample of air against a duplicate analysis of the same sample made with two samples of hydrogen just from the decomposing cell. Hydrogen was therefore sometimes used which had stood for a few days. Duplicate analyses were always made with different samples of hydrogen.

It may be observed that the corresponding measurements of different analyses were made under identical conditions. The calibration error, and the error caused by the imperfect parallelism of the reading microscope in its different positions, therefore, disappear from the *differences* of the analyses of different samples. The same is true of the error caused by the production of water in the

eudiometer between the second and third measurements in each analysis. No correction has been applied for this error, because the distribution of the water above and below the meniscus can not be easily determined. The amount of water adhering to the interior of the eudiometer before the commencement of an analysis has also been made always approximately the same. This has been accomplished by producing a vacuum in the eudiometer after the analysis, and the letting the mercury rise in it with a determinate velocity; when the eudiometer is clean, considerable uniformity is thus obtained.

In making observation as accurate as is required for my purpose, it is very important to keep the interior of the eudiometer very clean. A little irregularity in the film of water through which the meniscus is seen will spoil the reading. My eudiometer tube is cemented into a brass fitting which rests in a seat ground for it in the bottom of the enveloping box mentioned before. The eudiometer can be disconnected, removed, washed with caustic potash and shot, rinsed out with dust-free distilled water, and replaced ready for analysis, in an hour. The accurate fitting of the ground seat makes it possible to restore the zero of the graduation on the tube to the same level within the two hundredth of a millimetre, without even the bestowal of any thought on the matter. With this facility, the eudiometer has been kept sufficiently clean for accurate reading.

It is of course possible that the mean of all my analyses with the new apparatus is affected with a measurable constant error, though no measurable error has yet been traced to any assignable source. But it is certain that the differences in the means for different periods are affected with but very small errors. During the most favorable conditions under which I have used the apparatus, taking seventy minutes for each pair of analyses of the same sample, the mean error of a single analysis was, for half a month, less than the thousandth part of one per cent. Having commonly to work at odd times, and more rapidly than this, the accuracy attained has been less; but, for the whole seven hundred and eighty-eight analyses made with it, the mean error of a single analysis has been less than the two hundred and eightieth of one per cent. If, then, two samples of air differ by one-fiftieth of one per cent. in their contents of oxygen, the fact of a difference can be detected with a degree of probability nearly approaching certainty, at an expenditure of time not exceeding one hour for each sample.

NOTICE OF A PHOSPHORUSOXYIODIDE.

By Beverly S. Burton.

Having frequently observed, on closely examining the residue in the retort after preparing ethyl iodide, minute golden scales, I was induced to examine these more closely. To this end the residue was treated with water and filtered from the excess of red phosphorus; the filtrate was then evaporated on the water-bath.

When quite concentrated, and allowed to cool, a quantity of granular red crystals was deposited, which were purified by drying on filter paper and recrystallization until all free iodine was perfectly removed. On one occasion the crystals were obtained much larger, with brilliant facets; the form was not determined. It is very soluble in water, alcohol and ether, the solution being perfectly colorless. This property is made peculiarly striking when the dish is simply wet with the solution and placed on the water-bath, thus becoming almost instantly a deep orange color to a beautiful scarlet, which again disappears when held a moment in the steam.

On heating, the crystals melt to a deep reddish brown crystalline mass; the melting point being 140°.

By increasing the heat, yellowish vapors are given off which blue starch-paper. These vapors condense on a cold surface as a yellowish red crystalline deposit, which behaves in all respects as the original body, *i. e.* sublimes, in part, unaltered.

The portions used in the further examination were purified perfectly from all free iodine and dried over sulphuric acid. It being found that a solution of the body was completely decomposed by silver nitrate, the method of analysis was the following:

An excess of silver nitrate was added to the solution, the separated silver iodide filtered off, and the excess of silver in the filtrate separated by hydrochloric acid. To the filtrate, free from silver, an excess of sodium carbonate was added, also a little sodium nitrate, then the whole evaporated to dryness and fused. The solution of the fused mass then precipitated with magnesia mixture; any alumina or silica, which might separate on addition of ammonia, being previously removed.

The following results were obtained:

	I.	II.
I	77·93	77·44
P	9.66	9.71
O	12.41	12.85
	100.00	100.00

corresponding to the formula $I_6P_2O_5$. On one occasion this body was also observed in the residue from the preparation of fuming hydriodic acid; it was extracted, purified, and the analysis made as above described, yielding the following:

I	81.91	81.88
P	8.36	8.22
O	9.73	9.90
	100.00	100.00

corresponding to I_9PO_2, or for better comparison with the above, $I_6P_4O_5$.

As it was considered not improbable that hydrogen might enter into its composition, a combustion was made, the substance being introduced in a boat before which was laid copper oxide, a long layer of lead chromate and a silver spiral, but the amount found was too minute to be regarded.

I would mention here that in the preparation of methyl iodide the same body is apparently formed; but on attempting to purify in the same manner, a brown residue remained on treating with water. This was filtered off, and on evaporating the filtrate the crystals before noticed were not formed, but yellow flocks resembling freshly precipitated arsenic sulphide separated, which behaved very differently from that previously obtained.

An attempt to prepare this compound was made by leading phosphine gas evolved by the action of water upon phosphonium iodide, into a solution of iodine in hydriodic acid, but so far without success. Owing to the very small quantities at disposal, and the want of a method of preparation, its more exact constitution cannot be given. As at present no definite formula seems to be indicated, any speculations as to the nature of this body, or whether possibly two or more exist, are premature.

Its further study will be continued at the earliest opportunity.

REVIEWS AND REPORTS.

Artificial Indigo.

Though the chemical processes involved in the artificial production of indigo have already been brought before the attention of the readers of this Journal, the following extracts from a lecture by Professor Roscoe, delivered before the Royal Institution of Great Britain, will not be without interest, as a number of facts connected with the industry of dyeing with the artificial dye-stuff are made public for the first time in the lecture.

After speaking of the discovery of indigo and the methods used for extracting the dye-stuff from the plant, the lecturer recounts the steps which have led to the discovery of the constitution of indigo, and consequently to its synthesis. These are:

Step No. 1.—This was made so long ago as 1840, when Fritsche proved that aniline, $C_6H_5NH_2$, can be obtained from indigo. The name for this now well-known substance is indeed derived from the Portuguese "anil," a word used to designate the blue color from indigo. This result of Fritsche's is of great importance, as showing that indigo is built up from the well-known benzene ring C_6H_6, the skeleton of all the aromatic compounds, and, moreover, that it contains an amido-group.

Step No. 2 was also made by Fritsche in the following year, when, by boiling indigo with soda and manganese dioxide, he obtained ortho-amido-benzoic acid, or, as he then termed it, anthranilic acid. The following is the reaction which here occurs:

$$\underset{\text{Indigo.}}{C_8H_5NO} + O + 2H_2O = \underset{\substack{\text{Ortho-amido-}\\\text{benzoic acid.}}}{C_7H_5NH_2O_2} + \underset{\substack{\text{Formic}\\\text{acid.}}}{CH_2O_2}$$

What light does this fact shed upon the constitution of indigo? It shows (1) that one of the eight atoms of carbon in indigo can be readily separated from the rest; (2) that the carboxyl and the amido-group are in neighboring positions in the benzene ring, viz. 1 and 2.

Step No. 3.—The next advance of importance in this somewhat complicated matter, is the discovery by Erdmann and Laurent independently, that indigo on oxidation yields a crystalline body, which, however, possesses no coloring power, to which they gave the name isatin.

$$\underset{\text{Indigo.}}{C_8H_5NO} + O = \underset{\text{Isatin.}}{C_8H_5NO_2}$$

STEP No. 4.—The reverse of this action, viz., the reduction of isatin to indigo, was accomplished by Baeyer and Emmerling in 1870 and 1878, by acting with phosphorus pentachloride on isatin, and by the reducing action of ammonium sulphide on the chloride thus formed.

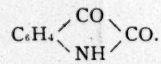
Understanding now something of the structure and of the relationships of the body which we wish to build up, let us see how this edifice has, in fact, been reared. Three processes have been successfully employed for carrying out this object. But of these three only one is of practical importance.

For the sake of completeness, let us, however, consider all three processes, although Nos. 1 and 2 are at present beyond the pale of practical schemes.

These three processes have certain points in common. (1) They all proceed from some compound containing the benzene nucleus. (2) They all start from compounds containing a nitrogen atom. (3) They all commence with an ortho-compound.

They differ from one another, inasmuch as No. 1 starts from a compound containing 7 atoms of carbon (instead of 8), and to this, therefore, one more atom must be added; process No. 2, on the other hand, starts from a body which contains exactly the right number (8) of carbon atoms; whilst No. 3 commences with a compound in which 9 atoms of carbon are contained and from which, therefore, 1 atom has to be abstracted before indigo can be reached.

Process No. 1 (Kekulé, Claissen and Shadwell).—So long ago as 1869 Kekulé predicted the constitution of isatin, and gave to it the formula which we now know that it possesses, viz.:



Following up this view, Claissen and Shadwell, two of Kekulé's pupils, succeeded in preparing isatin, and, therefore, now indigo from ortho-nitro-benzoic acid.

The following are the steps in the ascent:

1. Ortho-nitro-benzoic acid acted on by phosphorus pentachloride yields the chloride $C_6H_4(NO_2)COCl$.

2. This latter heated with silver cyanide yields the nitril $C_6H_4(NO_2)CO.CN$.

3. On heating this with caustic potash it yields ortho-nitrophenyl-glyoxylic acid, $C_6H_4(NO_2)CO.CO_2H$.

4. This is converted by nascent hydrogen into the amido-compound $C_6H_4(NH_2).CO.CO_2H$.

5. And this loses water and yields isatin, $C_6H_4NH.CO.CO$.

(*Q. E. D.*)

The reasons why this process will not work on a large scale are patent to all those who have had even a bowing acquaintance with such unpleasant and costly bodies as phosphorus pentachloride or cyanogen.

Process No. 2.—Baeyer's (1878) synthesis from ortho-nitro-phenyl-acetic acid.

This acid can be obtained synthetically from toluene, and it is first converted into the amido-acid, which, like several ortho-compounds, loses water, and is converted into a body called oxindol, from which isatin, and, therefore, indigo, can be obtained. The precise steps to be followed are:

1. Ortho-amido-phenyl-acetic acid yields oxindol:

$$C_6H_4\begin{cases}CH_2.CO_2H\\NH_2\end{cases} = C_6H_4\begin{cases}CH_2\\NH\end{cases}CO + H_2O.$$

2. This on treatment with nitrous acid yields nitrosoxindol:

$$C_6H_4\begin{cases}CH(NO)\\NH\end{cases}CO.$$

3. This again, with nascent hydrogen gives amidoxindol:

$$C_6H_4\begin{cases}CH(NH_2)\\NH\end{cases}CO.$$

4. Which on oxidation gives isatin:

$$C_6H_4\begin{cases}CO\\NH\end{cases}CO$$

(*Q. E. D.*)

This process, the feasibility of which had also been foreseen by Kekulé, is, however, not available as a practical scheme, for various reasons.

Process No. 3.—This may be called the manufacturing process, and was also proposed by Baeyer. It starts from cinnamic acid, a substance contained in gum benzoin, balsam of Peru, and some few other aromatic bodies. These sources are, however, far too expensive to render this acid, thus obtained, available for manufacturing purposes. But Bertagnini, in 1856, had obtained cinnamic acid artificially from oil of bitter almonds, and other processes for the same purpose have since been carried out. Of these, that most likely to be widely adopted is the following practical modification by Dr. Caro of Mr. Perkin's beautiful synthesis of cinnamic acid:

1. $\underset{\text{Toluene.}}{C_6H_5CH_3} + 4Cl = \underset{\text{Benzylene dichloride}}{C_6H_5CHCl_2} + 2HCl.$

2. $\underset{\text{Benzylene dichloride.}}{C_6H_5CHCl_2} + 2\underset{\text{Sodium acetate.}}{CH_3COONa} =$

$$\underset{\text{Cinnamic acid.}}{C_6H_5CH{=}CH.COOH} + 2NaCl.$$

But why did Baeyer select this 9-carbon acid from which to prepare indigo? For this he had several reasons. In the first place it had long been known that all indigo compounds, when heated with zinc dust, yield indol, C_8H_7N, a body which stands therefore to indigo in the same relation as anthracen to alizarin, and Baeyer and Emmerling had so long ago as 1869 prepared this indol from ortho-nitro-cinnamic acid, thus :

$$C_6H_4(NO_2)CO_2H = C_8H_7N + O_2 + CO_2.$$

Secondly, the ortho-nitro-cinnamic acid required (for we must remember that indigo is an ortho compound and also contains nitrogen) can be readily prepared from cinnamic acid, and this itself again can be obtained on a large scale. Thirdly, this acid readily parts with one atom of carbon, and thus renders possible its conversion into 8-carbon indigo.

The next steps in the process are (3) the formation of ortho-nitro-cinnamic acid; (4) the conversion of this into its dibromide; (5) the separation from this of two molecules of hydrobromic acid, giving rise to ortho-nitro-phenylpropiolic acid, and (6) lastly, the conversion of this latter into indigo by heating its alkaline solution with grape sugar, xanthate of soda, or other reducing agent. These reactions are thus represented :

3. $C_6H_5CH=CH.COOH$ yields $C_6H_4(NO_2)CH=H.COOH$.
Cinnamic acid. Ortho-nitro-cinnamic acid.

In this process the para-acid is also obtained, and, as this is useless for the manufacture of indigo, it has to be removed. This is effected by converting the acids into their ethyl-ethers, which, possessing different degrees of solubility, can be readily separated from one another.

4. This is next converted into the dibromide,

$$C_6H_4(NO_2)CHBr.CHBr.COOH.$$

5. And by careful treatment with caustic soda this yields ortho-nitro-phenylpropiolic acid, thus :

$$C_6H_4(NO_2)CHBr.CHBr.COOH + 2NaOH = C_6H_4(NO_2)C_2.COOH + 2NaBr + 2H_2O.$$

6. $n[C_6H_4(NO_2)C_2.COOH + H_2 = C_8H_5NO + CO_2 + H_2O$.
Ortho-nitro-propiolic acid. Indigo.

(*Q. E. D.*)

The last of these reactions is in reality not so simple as the equation indicates, for only about 40 per cent. of indigo is obtained, whereas, according to theory, 68 per cent. should result. Indeed, although, as we have seen, indigo can be prepared by these three methods, chemists are as yet in doubt as to its molecular weight, the probability being that the molecule of indigo contains twice 16

atoms of carbon, or has the formula $4(C_8H_5NO)$ or $C_{32}H_{20}N_4O_4$. Still, it must be remembered that, according to Sommaruga, the vapor-density of indigo is 9.45—a number corresponding to the simpler formula $C_{16}H_{10}N_2O_2$.

The artificial production of indigo may even now be said to be within reasonable distance of commercial success, for the ortho-nitro-phenyl-propiolic acid—the colorless substance which, on treatment with a reducing agent, yields indigo-blue—is already in the hands of the Manchester calico-printers, and is furnished by the Baden Company for alkali and aniline colors at the price of 6 shillings per lb. for a paste containing 25 per cent. of the dry acid.

With regard to the nature of the competition between the artificial and the natural coloring matters, it is necessary to say a few words. In the first place, the present price at which the manufacturers are able to sell their propiolic acid is 50 shillings per kilo. But 100 parts of this can only yield, according to theory, 68.58 parts of indigo-blue, so that the price of the artificial (being 73 shillings per kilo.) is more than twice that of the pure natural color. Hence, competition with the natural dye-stuff is not to be thought of until the makers can reduce the price of dry propiolic acid to 20 shillings per kilo. and also obtain a theoretical yield from their acid. This may, or it may not, be some day accomplished, but at present it will not pay to produce indigo from nitro-phenyl-propiolic acid. Nevertheless, a large field lies open in the immediate future for turning Baeyer's discovery to practical account. It is well known that a great loss of coloring matter occurs in all the processes now in use for either dyeing or printing with indigo. A large percentage of indigo is lost in the "cold vats" in the sediment. Another portion is washed off and wasted after the numerous dippings, whilst, in order to produce a pattern, much indigo must be destroyed before it has entered into the fibre of the cloth. Moreover, the back of the piece is uselessly loaded with color. In the processes of printing with indigo the losses are as great or even greater, and, in addition, such considerable difficulties are met with that only a few firms (Potter, Grafton in Manchester, and Schliefer in Elberfeld) have been successful in this process. But a still more important fact remains—that no printing process exists in which indigo can be in combination with other colors in the ordinary way, or without requiring some special mode of fixing after printing. Hence, it is clear that the weak points of natural indigo lie in the absence of any good process for utilizing the whole of its coloring matter, and in the impossibility, or, at any rate, great difficulty, of employing it in the ordinary madder styles of calico-printing. Such were the reasons which induced the patentees to believe that, although the artificial dye cannot be made at a price to compete with natural indigo for use in the ordinary dye-beck, it can even now be very largely used for styles to which the ordinary dye-stuff is inapplicable.

To begin with, Baeyer employed (Patent 1177) grape-sugar as a reducing agent. The reduction in this case does not take place in the cold, and even on long standing only small traces of indigo are formed, but if heated to 70° or upwards the change takes place. Unfortunately this production of indigo-blue is rapidly followed by its reduction to indigo-white, and it is somewhat difficult in practice to stop the reaction at the right moment. But "necessity is the mother of invention," and Dr. Caro, of Mannheim, to whom the speaker is greatly indebted for much of the above information, found that sodium xanthate is free from many of the objections inherent to the glucose reduction process, inasmuch as the reaction then goes on in the cold. Moreover, he finds that the red isomeride of indigo-blue, Indirubin, which possesses a splendid red color, also occurring in natural indigo, but whose tinctorial power is less than that of the blue, is produced in less quantity in this case than when glucose is employed. On this cloth alumina and iron mordants may be printed, and this afterwards dyed in alizarin, &c., or this coloring matter may also be printed on the cloth and the color fixed by moderate steaming without damage to the indigo-blue. This process is now in actual use by printers both in England and on the Continent, so that, thanks especially to the talent and energy of Dr. Caro, Baeyer's discovery has been practically applied within the short space of twelve months of its conception. Operations on a manufacturing scale have been successfully carried on in the Baden Soda and Aniline Works at Ludwigshofen for the last two months, and the directors see no reason why they should not be able to supply any demand, however great, which may be made for ortho-nitro-phenyl-propiolic acid.

The proper way of looking at this question at present is, therefore, to consider ortho-nitro-phenyl-propiolic acid and indigo as two distinct products not comparable with each other, inasmuch as the one can be put to uses for which the other is unfitted, and there is surely scope enough for both. Still, looking at the improvements which will every day be made in the manufacturing details, he must be a bold man who would assert the impossibility of competing with indigo in all its applications. For we must remember that we are only at the beginning of these researches in the indigo field. Baeyer and other workers will not stay their hands, and possibly other coloring matters of equal intensity and of equal stability to indigo may be obtained from other as yet unknown or unrecognized sources, and it is not improbable that these may turn out to be more formidable competitors in the race with natural indigo than ortho-nitro-phenyl-propiolic acid.

Looking at this question of the possible competition of artificial with the natural indigo from another standpoint of view, it must, on the other hand, be borne in mind that the present mode of manufacturing indigo from the plant is extremely rude and imperfect, and that by an improved and more careful carrying out of the pro-

cess great saving in coloring matter may be effected, so that it may prove possible to produce a purer article at a lower price, and thus to counterbalance the production of the artificial material.

The following are the directions issued by the patentees to calico-printers for using the new color:

Printing with Artificial Indigo.

No. I.—*On Unprepared Cloth.*

Standard.—Take 4 lbs. propiolic acid paste (equal to 1 lb. dry acid) and 1 lb. borax finely powdered; mix well. The mixture first becomes fluid and at last turns stiff. Then add 3 quarts white starch thickening (wheat starch); mix well, and strain.

Printing Color.—Take the above standard and dissolve in it immediately before printing 1½ lbs. xanthate of soda, stir well, and ready for use. For lighter shades reduce the above printing color with the following: In 1 gallon white starch paste dissolve 1 lb. xanthate of soda.

Directions for Use.—Print and dry as usual. The pieces ought not to be placed in immediate contact with drying cylinders, or otherwise subjected to heat above 100° C. The indigo-blue is best developed by allowing the printed goods to remain in a dry atmosphere and at an ordinary temperature for about forty-eight hours. Damp air ought to be excluded as much as possible until the color is fully developed. Then the pieces may be passed through the ageing machine, or steamed at low pressure if such treatment should be required for fixing any other color or mordant printed along with the indigo-blue.

After the blue is ready formed, the pieces are first thoroughly washed in the washing machine and *then boiled* in clean water, or better, in a weak solution of hyposulphite of soda (1 lb. to 10 gallons), *and at a full boil* for half an hour in order to volatilize the smell which would otherwise adhere to the goods.

Clean in a soap-bath, at a temperature not above 40° C.; wash, dry, and finish.

Observations.—Wheat starch gives the best results in the color, then follows gum tragacanth. The color is considerably reduced by using gum senegal, dark British gum, or calcined farina as thickening materials.

So far borax has answered best as an alkaline solvent of propiolic acid; it may, however, be replaced in the above standard by acetate of soda (from 1 to 1½ lbs.) or by 6 ozs. pearl-ash or soda. Any excess of caustic potash, or soda, destroys propiolic acid.

The above standard keeps unchanged for any length of time; it is likewise not sensibly altered by a small amount of xanthate of soda; but when mixed with its full proportion of xanthate, as in the above printing color, it gradually loses strength after several hours.

The xanthate ought, therefore, to be mixed with the standard immediately before printing, and any color remaining unused may then be saved by mixing with the same a large proportion of starch paste.

Propiolic acid may be printed along with aniline-black, catechu brown and drabs, and with alumina and iron mordants for madder colors.

After the indigo-blue is fully developed, the mordants are fixed in the ordinary manner, dyed with alizarin, padded with Turkey-red oil, steamed, and otherwise treated as usual.

Indigo-blue, whether natural or artificial, suffers by prolonged steaming at high pressure. For this reason only such steam colors can be associated with propiolic acid as may be fixed by short steaming at low pressure.

No. II.—*On Prepared Cloths (for Full Shades).*

Dissolve 2 lbs. of xanthate of soda in 1 gallon of cold water. Pad the goods with the above; dry, print with standard, and after printing follow the above treatment. The pieces may also be first printed with xanthate and then covered with standard. Alumina and iron mordants for madder colors may be likewise printed on cloth thus prepared, or printed with xanthate of soda.

The potential importance, from a purely commercial point of view, of the manufacture, may be judged of by reference to the following statistics, showing that the annual value of the world's growth of indigo is no less than four millions (pounds) sterling ($20,000,000).

Estimated Yearly Average of the Production of Indigo in the World, taken from a Total Crop for a Period of Ten Years.

	Pounds weight.	Pounds st'g.
Bengal, Tirhoot, Benares, and N. W. India	8,000,000	2,000,000
Madras and Kurpah	2,200,000	400,000
Manilla, Java, Bombay, etc.		500,000
Central America	2,250,000	600,000
China and elsewhere, consumed in the country,	say	500,000
		4,000,000

How far the artificial will drive out the natural coloring-matter from the market can not, as has been said, be foreseen. It is interesting, as the only instance of the kind on record, to cast a glance at the history of the production of the first of the artificial vegetable coloring-matters, alizarin. In this case the increase in the quantity produced since its discovery in 1869 has been enormous; such indeed that the artificial color has now entirely superseded the natural one, to the almost complete annihilation of the growth of

the madder-root. It appears that while for the ten years immediately preceding 1869 the average value of the annual imports of madder-root was over one million sterling ($5,000,000), the imports of the same material during last year (1880) amounted only to £24,000 ($120,000); the whole difference being made up by the introduction of artificial alizarin. In 1868, no less a quantity than 60,000 tons of madder-root were sent into the market, this containing 600,000 kilos of pure natural alizarin. But in ten years later a quantity of artificial alizarin, more than equal to the above amount, was sent out from the various chemical factories. So that in ten years the artificial production had overtaken the natural growth, and the 300,000 or 400,000 acres of land which had hitherto been used for the growth of madder, can henceforth be better employed in growing corn or other articles of food. According to returns, for which the speaker had to thank Mr. Perkin, the estimated growth of madder in the world previous to 1869 was 90,000 tons, of the average value of £45 ($225) per ton, representing a total of £4,050,000 ($20,000,000).

Last year (1880) the estimated production of the artificial coloring-matter was 14,000 tons, but this contains only 10 per cent. of pure alizarin. Reckoning 1 ton of the artificial coloring-matter as equal to 9 tons of madder, the whole artificial product is equivalent to 126,000 tons of madder. The present value of these 126,000 tons of alizarin paste, at £122 per ton, is £1,568,000. That of 126,000 tons of madder at £45 is £5,670,000, or a saving is effected by the use of alizarin of considerably over four millions sterling. In other words, we get our alizarin dyeing done now for less than one-third of the price which we had to pay to have it done with madder.

* * * * * * * * * * * *

To Englishmen it is a somewhat mortifying reflection, that whilst the raw materials from which all these coal-tar colors are made are produced in our country, the finished and valuable colors are nearly all manufactured in Germany. The crude and inexpensive materials are, therefore, exported by us abroad, to be converted into colors having many hundred times the value, and these expensive colors have again to be bought by English dyers and calico-printers for use in our staple industries. The total annual value of manufactured coal-tar colors amounts to about three and a half millions (pounds sterling); and as England herself, though furnishing all the raw material, makes only a small fraction of this quantity, but uses a large fraction, it is clear that she loses the profit on the manufacture. The causes of this fact, which we must acknowledge, viz., that Germany has driven England out of the field in this important branch of chemical manufacture, are probably various. In the first place, there is no doubt that much of the German success is due to the long-continued attention which their numerous universities have paid to the cultivation of organic

chemistry as a pure science. For this is carried out with a degree of completeness, and to an extent to which we in England are as yet strangers. Secondly, much again is to be attributed to the far more general recognition amongst German than amongst English men of business of the value, from a merely mercantile point of view, of high scientific training. In proof of this it may be mentioned, that each of two of the largest German color works employs no less a number than from twenty-five to thirty highly educated scientific chemists, at salaries varying from £250 to £500 or £600 per annum.

The Chemists at Cincinnati.

On the seventeenth day of August the American Association for the Advancement of Science met at Cincinnati, with President Geo. J. Brush in the chair. The Sub-section of Chemistry was well attended, but the chairman, Professor W. R. Nichols, was absent because of illness. The secretary, Professor Wiley, was also obliged to be absent a large part of the time, and accordingly Prof. G. C. Caldwell and Dr. Albert Springer served as chairman and secretary, respectively. During the meetings the Association adopted a number of amendments to its constitution; one of which elevated the Sub-section of Chemistry to the rank of a full section, and gave to its future chairmen the standing of Vice-Presidents of the whole association. For next year, Prof. H. Carrington Bolton will be the Vice-President over the new section C, and Dr. Springer Secretary.

The day preceding the meeting of the Association, the Society for the Promotion of Agricultural Science met. Before this body, several papers having chemical purport were read. One was by Professor Kedzie, on a vesiculating test for wheat-flour, and another by Professor Caldwell on the analysis of milk.

In the analysis of milk for agricultural purposes, only total dry substance, fat and protein are usually determined. In cases when it is desired to determine the average composition of the milk of a cow, or to test the effect of any special system of feeding on the quality of the milk, or to compare the milk of cows of different breeds, it is not sufficient, as has been shown by Kühn, to analyse the milk of one day, or even of several days distributed at intervals through a certain period; but the milk of every milking of several successive days must be examined.

To avoid the labor of so many separate determinations of dry substance, fat and protein, the writer sets out with a sufficient quantity of properly prepared sand, previously weighed in a weighed porcelain dish, to take up the residue of six or eight milkings: of

the first milking he adds about 10 cc. carefully weighed, and evaporates down to moderate dryness; this residue is set aside till the next milking, when another portion of 10 cc. is added and evaporated in like manner, and so on. Finally the whole is dried down to a point just short of brittleness, when it is carefully pulverized by means of a small pestle made of glass rod; great care is taken as each portion of milk is evaporated to scrape down the residue that adheres to the sides of the dish, with a small spatula made by flattening out the end of a piece of stout platinum wire, and to mix it with the sand. The pulverized residue finally obtained is dried as completely as possible over the water-bath, and then at 100° C. in the drying chamber for an hour, and finally for several days in the desiccator over sulphuric acid. Repeated analyses of a residue obtained and prepared in this manner have shown that it has a uniform composition throughout. It may be sealed up in a flask and kept, if desired, till a more convenient season for determination of fat and protein. The dry residue, fat and protein found give the average composition of the milk for the whole period of three or four days during which the milk was collected.

The writer next spoke briefly of the various methods for the quick determination of the fat for sanitary or technical purposes, and affirmed that all so-called optical methods of testing milk have failed to give satisfaction; that Marchand's lactobutyrometrical method has found increasing favor in the past two years; that Soxhlet's method, depending on the determination with a delicate areometer of the specific gravity of the etherial solution of the fat of the milk, obtained by shaking up definite quantities of the milk and ether together, with the addition of a little potash, gives remarkably accurate results, and promises to be of great utility in the hands of the intelligent dairyman, although the apparatus could not be so well trusted to clumsy hands as the lactobutyrometer. He showed that the formula for calculating the dry substance from the specific gravity and per cent. of fat, given by Behrend and Morgen in Journal für Landwirthschaft **27**, 249, while in most cases yielding very good results, may in some cases give such as are 0.7 per cent. from the correct proportion.

Finally he called attention to the fact that from the results of the very large number of analyses of milk made in Germany in 1879, it appears that milk may fall much below the standard generally accepted as the minimum and still be genuine milk, and gives his approval to the idea that Boards of Health should have the power to pronounce milk to be unfit for sale as good milk when it falls below a certain standard, without any regard to the question whether it was watered or not—that whether watered by giving the cow sloppy fodder, or by adding water to the milk of a properly fed cow, the final result is the same imposition on the public.

On Thursday, the eighteenth, the room of the chemical subsection was given up to the Association of Agricultural Chemists,

before whom a paper by C. M. Stillwell was read, on the "Preparation of samples for analysis." Henceforward this Association will not act as a separate organization, but will be a part of the regular Section of Chemistry.

The active work of the sub-section began on Friday, with a paper by C. W. Dabney, Jr., on "An Isopicraminic Acid." Following this, Professor A. B. Prescott read an essay of H. B. Parsons on "The Composition and Quality of American Wines," and Dr. Springer presented a communication upon "Pentachloramyl formate." A broad glass tube, bent to a quarter circle, was filled with amyl formate, and exposed during five or six days to the combined action of sunlight and a stream of dry chlorine. When the operation was completed the excess of free chlorine and hydrochloric acid were expelled by a current of dry carbon dioxide, and then the product was washed with water and carefully dried. Pentachloramyl formate, thus obtained, is a heavy, colorless liquid of sp. g. 1.52. It fumes considerably when exposed to the air, and has an irritating odor. Cold water does not decompose it in less than three weeks; but water at 70° does. Heated to 108° it becomes brown, and at 120° almost black; hence it cannot be distilled either by itself or with water. It has an acid reaction, and burns with a greenish flame. Exposed to light it undergoes decomposition in about three weeks; but in darkness the time was prolonged to seven weeks. Formula, $C_6H_7Cl_5O_2$. Dr. Springer thinks that in constitution it may be regarded as a chlorocarbonate of tetrachloramyl, from considerations based upon the properties of an ammonia salt derived from it. This salt is still under examination.

The fourth and fifth papers were by Dr. J. Lawrence Smith. First he described and exhibited a specimen of pig iron of uncertain origin, having anomalous chemical properties. It contained sixteen per cent. of silicon, and was absolutely unacted upon by acids. A polished fragment of it which had been long imbedded in iodine showed no signs of rust or corrosion. His other communication was upon the new mineral Hiddenite, of which he exhibited specimens, both uncut and mounted as a gem. Dr. Smith was followed by Miss Virginia K. Bowers, whose paper was entitled: "Is the Law of Repetition the Dynamic Law underlying the Science of Chemistry?" Professor A. B. Prescott next read upon "The limited biological importance of synthetic achievements in organic chemistry."

The solicitude shown for half a century as to the biological bearings of chemical synthesis arises from a misapprehension of the scope of chemical action. It must be accepted, from all we know of the sphere of chemism, (1) that the matter of protoplasm is at all events in a state of chemical combination, but (2) it cannot therefore be accepted that chemical union in itself supplies the essential conditions for organization or other vital functions. This is just the

question of abiogenesis, to be settled by experiment. Chemical action is distinct from organization, as, also, it is from cohesion, adhesion, heat, etc., and its co-relations to all these molecular activities always have to await demonstration.

So far, a cell-growth appears to be indispensable to the simple splitting of sugar into alcohol and carbon dioxide. There may or may not be an essential co-relation between cell-growths and proteid chemical syntheses. The growing vegetable cell may or may not be one of the conditions for the chemical formation of cellulose. The synthesis of the latter certainly can promise nothing of the inception of cell organization.

The closing paper of the day was by R. B. Warder, upon the "Evidence of atomic motion within liquid molecules, as based upon the speed of chemical action."

The experimental evidence upon which the argument of this paper is based has already been published; viz., the author's determinations of the speed of the saponification of acetic ether at different temperatures[1] and Weber's determinations of liquid diffusion.[2] The twenty determinations of speed of saponification just referred to agree pretty closely with an empirical formula of the form

$$a = A + Bt^3$$

where a denotes the "coefficient of speed," and t is the temperature of the mixture.

Weber, on the other hand, shows that the diffusion constant varies nearly according to the linear equation,

$$K = A' + B't.$$

Now when chemical action takes place in a very dilute solution, the solvent will often retard the action for hours or days; the unlike molecules cannot react upon each other unless they are brought very near together; and in what we call a homogeneous fluid this takes place by diffusion. Any change of conditions by which the diffusion is increased may likewise increase the speed of chemical action. But while the increase in the diffusion constant for dilute solutions varies nearly as the *first* power of the temperature, the increase of chemical action (in the case before us) is nearly as the second power of the temperature. From these facts I conclude that the increase in the rate of diffusion alone is not sufficient to account for the increased rate of chemical action, and a second cause for the increased speed of the reaction must be sought in the atomic motion within the liquid molecules. If the amplitude of the atomic vibrations is increased by raising the temperature (no matter what the nature of those vibrations may be), we must suppose that they recede further from the conditions of mean equilibrium,

[1] Ber. d. c. G. **14**, 1361. [2] Wied. Annal. **7**.

the stability of the molecule would most probably be diminished thereby, and the frequency of a metathesis would accordingly be increased, as shown by the determinations already referred to.

On Saturday, the following papers were read: "The Constitution of the Atom of Science," by Mrs. A. B. Blackwell. "An attachment for burettes avoiding the necessity of using glass stopcocks," by Professor F. A. Roeder. Professor Roeder also exhibited and described an interesting new form of analytical balance. Both of these communications were valuable, but neither could be made clear to readers without the use of diagrams. "Amylose; its nature and methods of analysis," by Professor H. W. Wiley. Later in the day the same chemist read upon the "Relation of reducing power as measured by Fehling's solution to the rotatory power of glucose and grape sugar." Dr. J. Lawrence Smith described a regulator for filter pumps, and Professor W. O. Atwater presented a communication on "The sources of the nitrogen of plants."

This paper gave the results of a series of experiments with plants grown in sand, to which known quantities of plant-food were supplied. The amount of nitrogen at the end of the experiment, *i. e.* in the plant and soil together, was greater than that supplied in seed and nutritive solution. The excess, which was equal to about one-fourth of the whole nitrogen of the plants, must have come from the air. The experiments do not prove, however, that this nitrogen was taken from the air by the foliage of the plants, though it is not easy to see how so large a quantity could have been absorbed by the nutritive solution and thus communicated to the plants through the roots. The experiments are being repeated with appliances for studying this latter question.

On Monday, August 22, the Sub-section of Chemistry finished up its work and adjourned. First, Professor Wiley read a paper upon "Mixed or New Process Sugars, with Methods and Results of Analyses." He was followed by Professor Henry Carmichael, with two communications—one on a "Filtration Evaporation Balance," and the other upon "The Liquefaction of Glass in Contact with Water at 250°C." Professor Wiley then described "A New Material suitable for Stop-Cocks and Stoppers for Reagent Bottles." This was the so-called "Mayall metal," made by T. J. Mayall, of Reading, Mass., which consists of 5 to 6 parts graphite, 1 part rubber and ½ part sulphur. Instead of sulphur, sulphide and antimony may be used. Next came papers by Professor W. O. Atwater, in abstract as follows:

The Chemistry of Fish and Invertebrates.—This paper gave a report of progress during the past year of an investigation which is being conducted under the auspices of the Smithsonian Institution and the U. S. Fish Commission, in the chemical laboratory of Wesleyan University, and of which an account was given at the Boston meeting of the Association.

The number of samples thus far analyzed is seventy-six, of which fifty-one are fish and twenty-five invertebrates, oysters, lobsters, etc. The investigation is to be reported in detail in the Report of the U. S. Fish Commission, and perhaps elsewhere.

The Quantitative Estimation of Chlorine.—The applicability of Volhard's method for the determination of chlorine in organic (animal and vegetable) compounds was tested by trials with known amounts of sodium chloride mixed with sugar, the mixture being fused with sodium carbonate and nitrate, the fusion dissolved in nitric acid, silver nitrate added in excess, and the latter determined with sulphocyanide solution by the method of Volhard. It appears that especial care is needed in the fusion; but, if this be conducted slowly and at a low temperature, there is no appreciable loss of chlorine. This done, the precautions mentioned by Volhard will, with proper manipulation, insure very accurate results. Direct determination of chlorine in the fusion by precipitation and weighing as silver chloride, as has been recommended, brings results far too low, on account of the solubility of silver chloride in sodium nitrate. The determination by Volhard's method is convenient and satisfactory.

Last of all came a communication by Professor G. C. Caldwell, on "Some New Forms of Laboratory Apparatus."

For a water-bath heated by steam the writer uses a strong cast iron box, about 5 inches deep and 6 inches broad and from 2 to 3 feet long, according to the number of water-baths to be heated, into which steam from the boiler is conducted, while the waste and condensed water is allowed to flow out through a narrow opening, regulated by a stop-cock in the bottom at the other end. Cup-like depressions 3 or 4 inches in diameter and 3 inches deep are sunk in this box from the upper surface, which communicate with a supply of water through pipes passing from the bottom of each cup and through the bottom of the box to a small main running along beneath the box; water slowly flowing through these cups, and through an outlet beyond them which is raised about as high as the middle of the cups, is easily kept constantly boiling by the steam circulating within the space around the cups.

For the determination of the specific gravity of liquids the writer fills a weighed pipette provided with a short and fine beak and an upper tube with very fine bore, with a volume of liquid occupying the space between the point below and a mark on the tube above; with the aid of a properly constructed clamp, for the detailed description of which we have no room, the pipette is easily and very accurately filled with a constant volume of any liquid at any ordinary temperature.

For hot filtration with the Bunsen pump, a funnel with a long neck is put first through a cork in the neck of a small bottle, about two-thirds of whose body has been cut off, in such a manner that the part of the bottle left surrounds the funnel nearly to its top;

the beak of the funnel is next passed through a cork in the tubulure of a bell jar; a short glass tube also passed through the same cork provides for connecting the interior of the bell jar with the pump. The space around the funnel is partly filled with water, a glass tube is carried from a flask to the bottom of this space where it ends in a fine jet; the bell jar is set on a ground-glass plate on which a beaker is placed to receive the filtrate, connection is made with the pump, water is boiled in the flask, and the steam driven over to the water around the funnel soon heats that to boiling, and the contents of the funnel are kept hot during the filtration; the water that accumulates around the funnel is quickly returned to the flask by removing the lamp for a moment.

For the student's Gooch's crucible, in short courses of quantitative analysis, when the purchase of a platinum crucible can hardly be afforded, the writer proposes to use a porcelain crucible made with only a narrow ledge around the bottom; on this ledge a perforated disk of thick platinum foil can be placed, and the asbestos will easily close all the interstices between the foil and the ledge on which it rests. Such crucibles can be furnished by German manufacturers at the same rates as ordinary crucibles of the same size.

The next meeting of the Association, under the presidency of J. W. Dunson, will be held in Montreal, beginning on the last Wednesday of August, 1882.

F. W. CLARKE.

A MANUAL OF SUGAR ANALYSIS, including the application in general of analytical methods to the sugar industry, with an introduction of the chemistry of cane-sugar, dextrose, levulose, and milk-sugar. By J. H. TUCKER, Ph. D. New York: D. Van Nostrand, 23 Murray Street, and 27 Warren Street.

The object of this book is to present, in easily accessible form, to the public directly or indirectly connected with the sugar interests of this country, the results of investigations on sugar analysis, collected from German, English and French writers. The book is a valuable one for students in chemistry taking special interest in the analysis of sugars, inasmuch as it gives all technical analytical methods in use at the present time in sugar factories and commercial laboratories.

The physical and chemical methods for determining various kinds of sugars are given complete, as are also the methods for the analysis of bone-black, a product so extensively used for its absorptive power for coloring matter, organic and inorganic salts, etc., in the course of the manufacture of different sugars.

The chemistry of sugar is treated in chapters I, II, III, and IV, which contain the literature of cane-sugar, dextrose, levulose, and milk-sugar, up to the present time, in a condensed form.

It is, however, to be regretted that Mr. Tucker, in speaking of the melassigenic action of salts upon solutions of cane-sugar, omitted mentioning the method of Scheibler, by which almost all saccharose (cane-sugar) can be separated from salts and organic nitrogenous substances that are met with in ordinary beet-root molasses. This method is extensively used in Europe, and consists in the separation of the saccharose as calcium sucrate. The salts and nitrogenous organic substances that remain unacted upon in the treatment of molasses with caustic lime are dissolved by alcohol of a specific strength.

Although caustic lime is mentioned as influencing the rotatory power of cane-sugar, it is not stated how calcium sucrate and other sucrates have to be treated in order to obtain correct results with the polariscope.

Chapter X, on the analysis of molasses and syrups, is not as exhaustively treated as one would expect, considering the number of publications on the subject, the methods in use for determining nitrogen, carbon, hydrogen and oxygen being entirely omitted. It would have added to the value of the book if it had been stated how the above-named elements, particularly nitrogen, are quantitatively and qualitatively determined and detected in sugar-house molasses and syrups; it being known that nitrogen is playing an important part in Vincent's process for manufacturing on a large scale trimethylamine in connection with the distillation of alcohol from fermented beet-root molasses. In most respects, however, the book can be cordially recommended.

C. FAHLBERG.

PHILADELPHIA, *October 5th*, 1881.

NOTES.

Colliery Explosions.

F. A. ABEL has experimented upon several samples of coal dust obtained from the Seaham Colliery after the explosion of September, 1880.

Some of the samples appeared to have been affected by heat; but the chemical and microscopical examinations did not indicate the part taken by the coal dust in producing and transmitting the explosion. With a view to ascertaining the influence which coal dust exerts upon explosions in mines, the apparatus devised by

Galloway was employed, with some modifications. Samples of the Seaham dust which contained the largest proportion of coal were the most sensitive in producing the ignition of fire-damp. Explosions were effected with them in air containing only 2.5 per cent. of fire-damp. One sample of dust which was third in order of sensitiveness contained the lowest proportion of coal of all the others. Experiments were accordingly undertaken which showed that perfectly non-combustible powders (*e. g.* calcined magnesia) are, when exposed to the heat of a flame, nearly as effective as the highly sensitive dusts in producing ignition of air and fire-damp, which may otherwise constitute a non-explosive mixture. A mixture of fire-damp and air, containing 2.75 per cent. of the former gas, was allowed to pass a flame for some time at a velocity of 600 feet per minute. No explosive effect was produced, but, when the mixture was caused to convey calcined magnesia, a feeble explosion resulted.

The conclusions reached from the experiments with the dusts from the Seaham and other mines are:

(*a*) "That coal dust in mines not only much promotes and extends explosions in mines by reason of the rapid inflammability of the finely-divided combustible, and of the readiness with which it becomes and remains suspended in air-currents"; but

(*b*) "That it may also be itself brought into operation as a fiercely-burning agent which will carry flame rapidly as far as its mixture with air extends, and will operate even as an exploding agent through the medium of a proportion of fire-damp in the air of the mine, the existence of which, in the absence of the dust, would not be attended by any danger."

(*c*) "That dust in coal mines, quite apart from any inflammability which it may possess, can operate in a distinct manner as a finely-divided solid in determining the ignition of mixtures of only small proportions of fire-damp and air, and consequently in developing explosive effects."

It also appears that the proportion of fire-damp which is necessary to cause an explosion is below that which can be detected by the most experienced observers.—(*Chemical News*, **44**, 16, 27, 39.)

C. P.

Constitution of Phosphonium and Arsenium Compounds.

V. Meyer and M. Lécco[1] observed that the compound of dimethyl-ethyl-amine with ethyl chloride is identical with the compound formed by the union of methyl chloride with diethyl-methyl-amine. This compound is thus shown to be atomic and the nitrogen contained in it quinquivalent.

A. Michaelis and A. Link, following the same train of thought, have extended their observations to similar compounds of phosphorus and arsenic.

[1] Ber. deutsch. chem. Gesel. **10**, 233.

The bases

$(C_6H_5)_2PCH_3$ $(C_6H_5)_2AsCH_3$
$(C_6H_5)_2PC_2H_5$ $(C_6H_5)_2AsC_2H_5$

were caused to unite with ethyl iodide or methyl iodide with the formation of the compounds,

$(C_6H_5)_2PCH_3.C_2H_5I$ $(C_6H_5)_2AsCH_3.C_2H_5I$
$(C_6H_5)_2PC_2H_5.CH_3I$ $(C_6H_5)_2AsC_2H_5.CH_3I$

Isomerism of the products would imply the trivalence of these elements, identity on the other hand would indicate that they are quinquivalent. Perfect identity of these iodides was observed, thus showing that phosphorus and arsenic are probably quinquivalent. (*Annalen der Chemie*, **207**, 193.)

Free Fluorine.

The nature of the substance with a strong odor which occurs in the colored variety of fluor-spar from Wölsendorf has frequently been the subject of discussion, but up to the present no satisfactory conclusion has been reached. OSCAR LOEW has recently suggested that the substance may be free fluorine. He has also performed some experiments with the view of testing the correctness of the suggestion. It has been shown by Schrötter that the odor is not destroyed at 310°; that the odor is markedly changed by rubbing the mineral with caustic potash; that rubbed with sulphur an odor of sulphur chloride is produced; and that, further, the substance in question sets chlorine free from sodium chloride and iodine from potassium iodide. To these observations Loew adds that, when the mineral is triturated with dilute caustic potash, a solution is obtained which instantaneously decolorizes a solution of indigo, just as a hypochlorite would do.

One kilogram of the mineral was triturated with ammoniacal water as long as the liquid showed an alkaline reaction. The filtrate was treated with sodium carbonate, evaporated, the residue together with concentrated sulphuric acid brought into a platinum vessel and this covered with glass. The apparatus was allowed to stand for some time at a temperature of 40–50°. The result was a very marked etching of the glass. This experiment is regarded by Loew as proving the correctness of his view.

As cerium occurs in the fluor-spar from Wölsendorf, the hypothesis is put forward that the free fluorine is a result of the dissociation of cerium fluoride, the latter substance having, in all probability, originally been deposited with the calcium fluoride.—(*Ber. deutsch. chem. Gesell.* **14**, 1144.)

On the Occurrence of Free Fluorine.

As regards the possible formation of fluorine from cerium fluoride (see preceding note) K. BRAUNER calls attention to the fact that we know nothing about the properties of cerium tetrafluoride, the compound which Loew had in mind, nor do we even know that it exists. Further, it is known that most varieties of fluor-spar lose their color when heated, and, as the Wölsendorf mineral is strongly colored, it is probable that it has never been heated to a high temperature. Brauner has for some time been engaged in the study of the fluorides which correspond to the peroxides. Two of these are of importance for this discussion, viz. cerium tetrafluoride, $CeF_4 + H_2O$, and its double salt, $3KF.2CeF_4 + 2H_2O$. When the former salt is heated to dark red, the lower fluoride is left:

$$CeF_4.H_2O = CeF_3 + H_2O + F, \text{ or}$$
$$2(CeF_4.H_2O) = 2CeF_3 + 2HF + O + H_2O.$$

If the tetrafluoride is heated at first gently to drive off the water, and afterwards in a covered crucible to a somewhat higher temperature, the gas in the crucible has a very characteristic odor, quite different from that of hydrofluoric acid. The odor is so very like that of chlorine and hypochlorous acid, that some chemists who witnessed the experiment and had knowledge of the nature of the gas were firmly of the opinion that it was chlorine.—(*Ber. deutsch. chem. Gesell.* **14**, 1944.)

On the Petroleum from the Caucasus.

In a former communication attention was called to the researches of BEILSTEIN and KURBATOW on the petroleum obtained from Baiku on the Caspian sea. The oil was found to differ from the American in containing addition products of the aromatic hydrocarbons of the general formula C_nH_{2n}, examples of which are hexahydrobenzene, C_6H_{12}, hexahydrotoluene, C_7H_{14}, etc. The same chemists have now examined the petroleum from the wells belonging to the firm of Siemens and Halske, at Zarskije Kolodzy in the centre of the Caucasus. They separated the oil into three portions boiling respectively at 30–35°, 70–75° and 95–100°. The first fraction consists of pentane, the second of hexane and the third of heptane. The presence of benzene and toluene was also proved. Hence it is seen that the petroleum from the central Caucasus has a different composition from that obtained from the neighborhood of the Caspian sea. It consists essentially of the hydrocarbons C_nH_{2n} which also occur in American petroleum, and contains in addition small quantities of the aromatic hydrocarbons C_nH_{2n-6} (which have also been detected in Hannoverian petroleum) and of the hydrocarbons C_nH_{2n} first found in the petroleum from Baiku.—(*Ber. deutsch. chem. Gesell.* **14**, 1620.)

Commercial Petroleums.

OGLOBLINE has been engaged in an examination of petroleum from different sources, and his results are summed up thus. Although the specific gravity of the American petroleum is less than that of the Caucasian, the former contains a greater proportion of heavy oils. Both varieties emit inflammable vapor at so low a temperature that their use in the crude state is attended with danger. The Caucasian oil is not more difficult to purify than the American, and it is superior to the latter as an illuminating agent. As far as expense and intensity of light are concerned, the Caucasian oil burns better with a flat wick, the American oil with a round wick; the height of the end of the wick above the surface of the oil has a much greater effect on the illuminating power of the latter than on that of the former.—(*Bull. Soc. chimique*, [2], **34**, 682.)

Artificial Production of Crystallized Quartz.

Crystallized quartz has several times been prepared artificially: first by Sénarmont, who obtained it by heating gelatinous silica with hydrochloric acid; then by Daubrée, by the action of superheated water on glass; and lastly, by Hautefeuille, who treated silica at 750–800° with sodium tungstate. C. FREIDEL and E. SARASIN have now prepared it by heating to a temperature below dull redness in a closed steel tube lined with copper, a mixture of potash, alumina, and gelatinous silica, the last in excess, in presence of water. In this way, after continuing the heat, in one experiment for 14 and in another for 38 hours, they obtained silica wholly or almost wholly crystallized.

The first experiment yielded numerous very regularly formed crystals of the ordinary quartz form (prism with the two rhombohedrons), which acted strongly on polarized light in the manner of native quartz. In the second experiment the crystals were larger (up to 0.5 mm. long, and 0.1 mm. broad), but mostly broken off at one end. They sometimes had the form of more acute rhombohedrons, with indications of tetartohedral forms, and many of them exhibited striations and modes of aggregation well known in native quartz.—(H. W. in *Journal Chem. Soc.* from *Jahrbuch für Mineralogie*, 1880, **1**, 179.)

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